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CAM ANNUAL REPORT

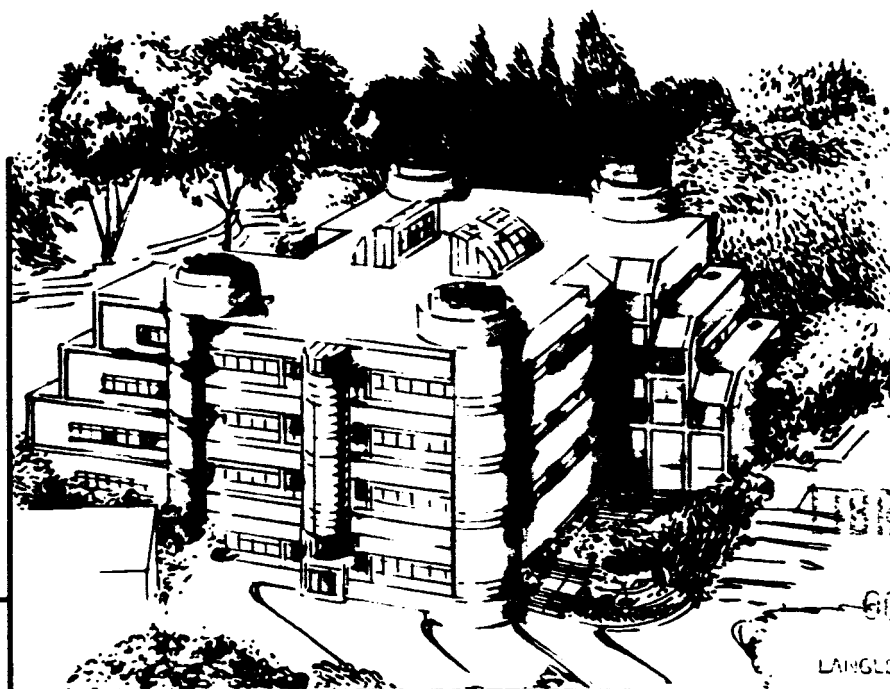
1986

**SURFACE SCIENCE AND CATALYSIS
ELECTRONIC MATERIALS
CERAMIC AND METAL INTERFACES
STRUCTURAL MATERIALS
INSTRUMENTATION FOR SURFACE SCIENCE
POLYMERS AND COMPOSITES**

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**Materials and Chemical Sciences Division
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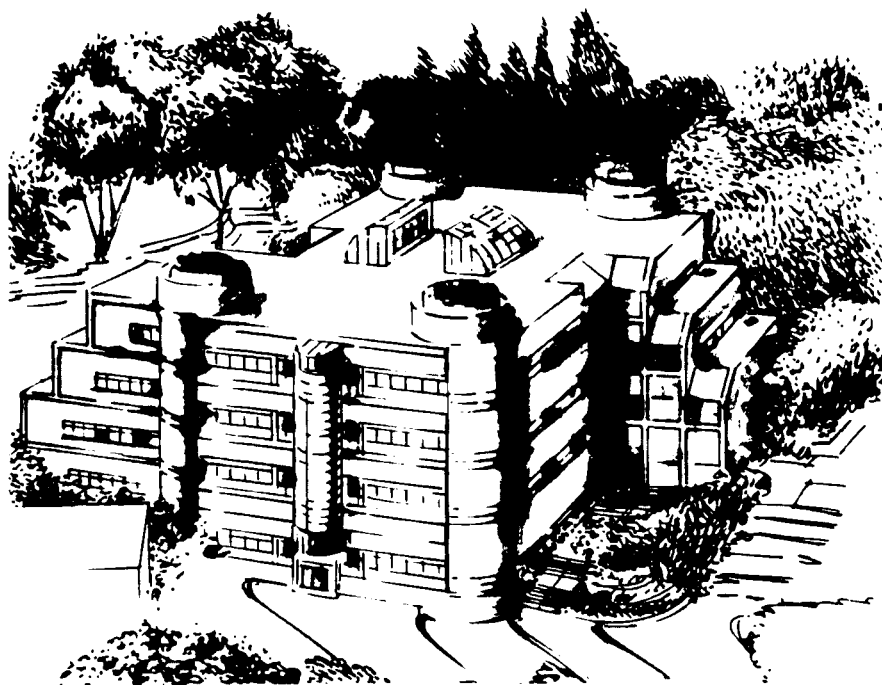
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Annual Report Production
Sally Nasman, Jeri Edgar, and Marilyn Graham

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FOREWORD

The Center for Advanced Materials (CAM) was established in October 1983. Its goal is to marshal the basic materials research capability of the Lawrence Berkeley Laboratory and the University of California, Berkeley, and bring it to bear on materials problems confronting U.S. industry. Thus CAM was one of the first responses to the now widely recognized need to assist the private sector in its competitive standing in world markets. In many ways it is expected to serve as a model for university-laboratory-industry cooperation to solve basic research problems of national importance.

Lawrence Berkeley Laboratory and the University of California have had a long history of productive research in materials science. The Center for Advanced Materials complements this continuing effort. Existing LBL materials research has, for the most part, taken the form of small, single-investigator groups working primarily with graduate students and postdoctoral research associates. The research problems addressed have been those involving materials of great scientific interest and perhaps long term application. On the other hand, programs at the Center are large, interdisciplinary and focused on specific areas in materials science that have been identified as critical by U.S. industry. Its results are expected to be of benefit within a 5-15 year period.

CAM investigators are currently pursuing six major areas of research:

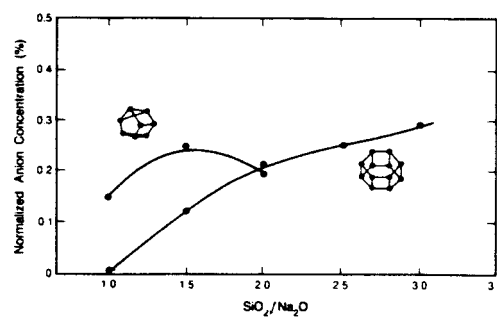
- Electronic Materials
- Polymers and Composites
- Instrumentation for Surface Science
- Surface Science and Catalysis
- Ceramic and Metal Interfaces
- Structural Materials

Support for this research comes primarily from the Division of Materials Sciences in the Office of Energy Research of the United States Department of Energy. Research on materials for high field superconducting magnets is supported by the Office of Magnetic Fusion Energy of the Department of Energy. Industrial support, in the form of unrestricted gifts, contracts, gifts of equipment and materials, is becoming an important source of additional funding. Close interactions with U.S. industry through workshops, advisory boards, and frequent and reciprocal visits provide CAM scientists with an understanding of the materials needs in the community and create efficient routes for transmitting research results back to industrial research laboratories for further development and application.

Another mission of the Center is the education of future generations of materials scientists and engineers. Our very close interaction with the University of California, Berkeley facilitates this effort. At the present time, 76 Berkeley graduate students are working on CAM projects. During our first three years, 26 students received their masters or doctoral degrees and six completed their postdoctoral training. Of this group, 21 have moved on to industrial research positions, and eight more have taken teaching positions in such institutions as Harvard, Wellesley, and Michigan Technological University. Others are continuing their studies.

Currently housed in a number of widely separated laboratory buildings, the CAM programs will soon move to two new laboratory buildings, the Surface Science and Catalysis Laboratory Building in September 1987 and the Advanced Materials Laboratory (a model of which is shown on the cover of this report) in March 1989.

This, our first annual report, reviews highlights of scientific and industrial activity in each of our six programs. A complete bibliography follows each section. We welcome comments, visits, and proposed collaborations, especially from industrial research laboratories.



SURFACE SCIENCE AND CATALYSIS

SURFACE SCIENCE AND CATALYSIS

The Surface Science and Catalysis Program is designed to develop, through basic research, the scientific foundation that will assist industries in a wide variety of areas of endeavor to develop new and improved surface materials and processes. Current research interests, as defined through discussions with industry representatives at the program workshop in 1983, are focussed in two areas:

- Heterogeneous Catalysis
- Coatings

Work in heterogeneous catalysis is centered on the synthesis and characterization of microporous crystalline materials including zeolites and transition metal carbides and nitrides. In the field of coatings research is focussed on plasma assisted deposition of hard coatings including titanium nitride and hard carbon and on the production of surface compounds that form at metal-oxide and metal-metal interfaces. The interface properties are characterized with a combination of modern surface science techniques.

Major recent accomplishments of the program include:

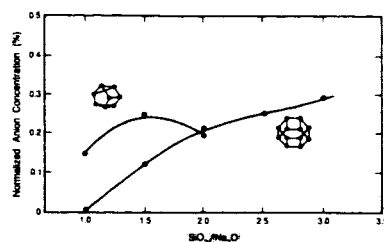
- A catalytic micro-reactor has been constructed inside the cavity of a NMR apparatus. This has allowed the continuous observation of microporous crystalline zeolites catalyzing reactions of interest.

- NMR spectroscopy has also been used to gain a better understanding of the sequence and mechanisms of the combination of silica and/or alumina subunits in the liquid phase prior to nucleation of microporous crystalline zeolites. This work has evoked considerable interest because it may lead to the synthesis of novel zeolites of predetermined structure through the rational control of the reaction conditions.

- Transmission electron microscopy is a commonly employed tool in the study of zeolite structures. Structure damage however frequently occurs due to electron irradiation during these studies. It has been found that high resolution imaging can determine structure even when radiation damage has occurred and this finding has greatly extended the utility of this tool.

- A scanning tunneling microscope has been constructed and studies have begun to provide a better characterization of the atomic structure and morphology of surfaces and interfaces.

- Hard titanium nitride coatings have been produced on M-2 tool steel by plasma assisted chemical vapor deposition.



The conditions of depositions were correlated with the composition, structure and mechanical properties of the titanium nitride deposit. Adhesion and interface composition at the failure regions have been correlated.

HETEROGENEOUS CATALYSIS

Microporous Crystalline Materials

This project brings an interdisciplinary approach to the synthesis and characterization of microporous crystalline materials. It seeks a better understanding of the relationship of zeolite synthesis to the character of the zeolites produced, and the effect of composition and crystallography on shape-selective properties and the number of acid sites and their acid strengths. This will contribute to the manufacture of new and better catalysts for a wide variety of purposes.

In work partially supported by the W. R. Grace and Company, ^{29}Si NMR spectroscopy has been used successfully to identify and measure quantitatively the siliceous species present in the magma from which zeolites A and Y are grown. The spectra obtained with a high-resolution 500 MHz spectrometer indicate the presence of monomeric silicate anions and oligomeric species containing 2 to 12 Si atoms linked via siloxane bridges. Thus far, 19 distinct structures have been identified, many of which contain 3, 4, and 6 membered rings. The presence of zeolite secondary building units, such as the cubic octamer and double hexamer, have also been established (Figures 1 and 2). For a fixed silica concentration the absolute concentration of a given species is a sensitive function of $\text{SiO}_2/\text{Na}_2\text{O}$ ratio.

A catalytic microreactor has been constructed inside the cavity of an NMR machine. This has opened up the ability to observe species present on the catalyst surface during reaction.

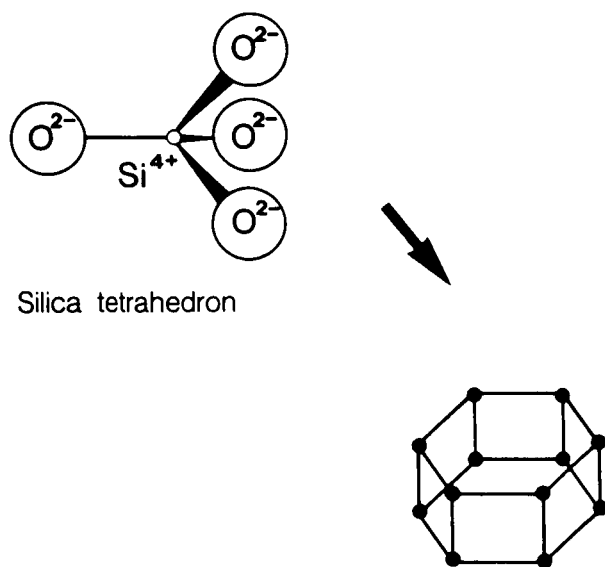


Figure 1.
Double hexamer. Only Si atoms are connected. Each Si atom shares four O atoms.

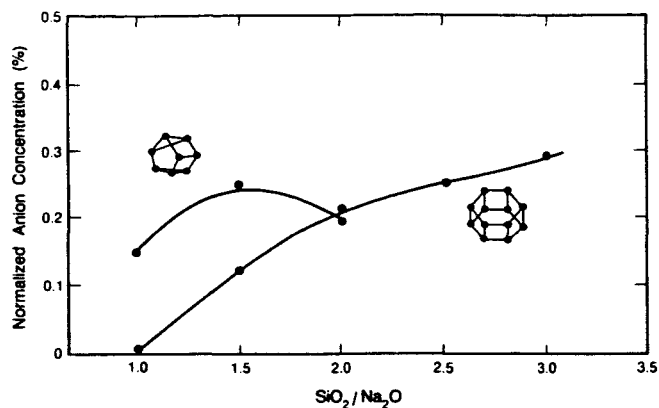


Figure 2.
Normalized concentrations of hexacyclic octamer and double hexamer as a function of silicate ratio.

A systematic study of the stability of zeolite Y during electron irradiation in the transmission electron microscope (TEM) has also been completed. The microscope accelerating voltage was varied from 80 kV to 200 kV to change the energy of the incident electrons and the Si/Al ratio of the specimens was varied in the three stages, 2.4, 18, and ∞ . This study led to the proposal of a mechanism for the damage of aluminum-containing zeolites in the TEM. The proposed mechanism explains the importance of the cation species (and water incorporation) in the degradation process.

Computer simulation of high resolution images has shown that even when the zeolite crystal has been degraded by the electron beam to a state where it is < 40% amorphous, there is very little loss of information about the crystalline structure (Figure 3). This represents a hopeful prognosis for performing electron microscopy even on the more beam-sensitive zeolites.

During the coming year, these techniques will also be applied to the study of crystalline materials having potential shape-selective characteristics such as crystalline aluminum phosphates and titanium silicates.

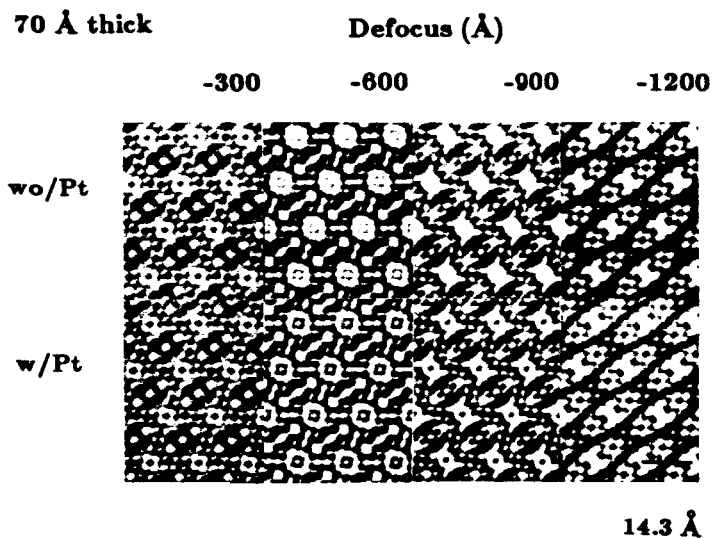


Figure 3.
High resolution imaging of zeolite Y with and without Pt present. Defocus of -900 Å shows the differences between two samples.

Metal Nitrides and Carbides

Work is also underway on the investigation of novel routes to synthesis of metal nitrides and carbides. A primary objective is to produce medium to high surface areas powders ($10\text{--}100\text{ m}^2/\text{g}$) without using metal oxide as a starting material. The most successful technique thus far involves intercalation of a metal sulfide with NH_3 and subsequent heating in excess NH_3 to produce the metal nitride. Initial studies have shown that Ta_3N_5 powders with surface areas of $30\text{ m}^2/\text{g}$ can be readily produced from TaS_2 and TaS_3 . Interest in the nitrides and carbides as catalysts derives from the finding that these compounds can perform as catalysts with selectivity similar to those of precious metals although thus far not at the same conversion level.

Low Temperature Liquid Phase Catalysis

The program objective is to synthesize by novel organometallic methodology new monomeric, defined transition metal-containing molecular assemblies which may be polymerized to novel matrices with which to execute new catalytic reactions. The principal aim is to generate structures of the type shown in Figure 4 in which an organic polymeric π system is sandwiched between transition metal layers.

Progress has been made in the characterization of the structure of the cross linked poly(acrylamide/vinylpyridine) electrode films. These polymeric films consist of a heterogeneous three-dimensional network of polymer bundles and open microscopic pores. Permeability measurements were obtained from rotating disk electrode experiments. The porosity of these films varies in the range of 30% to 50% depending on the pH of solution and the loading of the film with negatively charged species. Porosity increased with decreasing pH due to protonation of pyridine groups and concurrent swelling of the polymer bundles. Incorporation of hexacyanoferrate ions into the protonated matrix results in a small decrease of its porosity. The influence of the cross-linking agent on the porosity of the gel films is under investigation.

A porous thin-film matrix of agarose has been developed and evaluated as an electrode coating for immobilization of electroactive reagents. The measurements of the film porosity have shown excellent properties of this novel matrix with respect to mass transport processes. A general scheme of reagent immobilization has been developed based on the entrapment of insoluble microscopic aggregates of ion-exchange polymers. An example of such a two-component system consisting of agarose entrapped Nafion with immobilized 4,4-bipyridyl cations has been synthesized and fully characterized. Its electron transport kinetics were shown to be more than an order of magnitude faster than those in plain Nafion films. This phenomenon is related to the

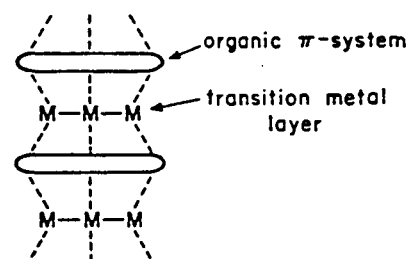


Figure 4.
Conducting Polymer

heterogeneous structure of these films and the coupling of the diffusion pathways between the solution and the polymer phases.

In addition, two synthetic approaches have been developed to the construction of monomers suitable for the polymerization to novel materials with alternating organic and metallic layers. The first is based on the synthesis of a trinuclear cobalt cluster containing an appended alkyne group, the second on the preparation of a unique π electron-rich ligand, 1,2,3,4,5,6-hexaethynylbenzene. The first system has been shown to be readily polymerizable to furnish a dark reactive polymer, the electrochemical and solid state properties of which are being investigated. A side-product in this polymerization is a linear trimer that constitutes a perfect model for a section of the polymer chain.

COATINGS

Plasma-excited molecules are currently used on a large scale to fabricate electronic devices through plasma-assisted deposition or etching processes. Hard coatings (nitrides, carbides) that impart favorable mechanical properties can be produced by plasma deposition. Laser excitation is utilized to produce naked metal clusters or other unusual molecules which then interact with surfaces in unexpected ways.

There is very little understanding of the excited state distribution of molecules in plasmas, the importance and abundance of molecular ions or even the chemical identity of molecules. Since the physical and chemical properties of the materials that form depend on the energy content and energy distribution in the excited molecules, correlating these properties is of great importance.

One application of plasmas is the promotion of the synthesis of hard coatings on tool steels below their tempering temperature. We have shown that the presence of a plasma accelerates the chemical vapor deposition of titanium nitride on M-2 steel from TiCl_4 and NH_3 at 400°C by an order of magnitude. If H_2 and N_2 are used instead of NH_3 , a plasma is essential for TiN formation. The hardness and scratch adhesion critical load values of our plasma assisted CVD films are comparable to line-of-sight deposition processes such as sputtering. The relationship between coating adhesion and interface composition is being investigated. An *in-situ* scratcher (Figure 5) with a diamond stylus was developed to create scratches in ultra high vacuum. Auger electron spectroscopy analysis of adhesive mode failures indicates that high chlorine concentrations are present. Strategies for investigating interfaces that do not easily fail are currently being explored.

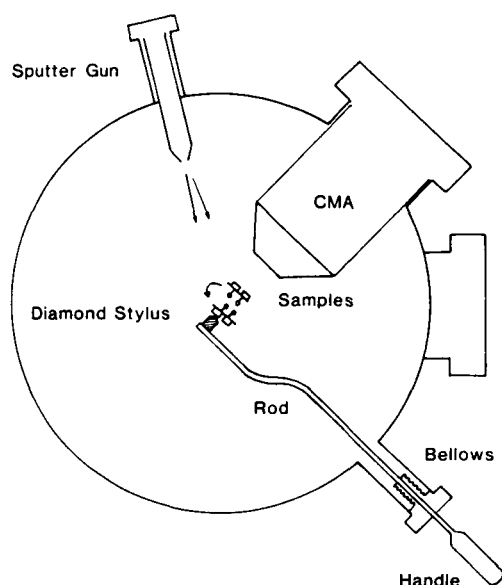


Figure 5.
In situ diamond scratcher for UHV
characterization of film-substrate
interface.

Surface Compounds

The objective of this project is to produce characterized surface compounds that form at metal-oxide interfaces of bimetallic monolayers. Their synthesis from plasma or laser excited molecules is also explored. The aim is to synthesize new materials that may be better catalysts, improved coatings or electronic devices. Focus is on atomic scale characterization of the structure, morphology and composition of the surface compounds and correlations with chemical, mechanical and electronic properties.

A major effort in this area involves the development of state-of-the-art instrumentation, including, for example, scanning tunneling microscopy to provide a better characterization of the structure and morphology of surface compounds (see Instrumentation for Surface Science Program). A first generation STM operating in air has been constructed and images of Au films deposited on mica and of Au crystal surfaces have been obtained with a vertical resolution of 0.5 Å (Figure 6). The instrument will be used to study the growth

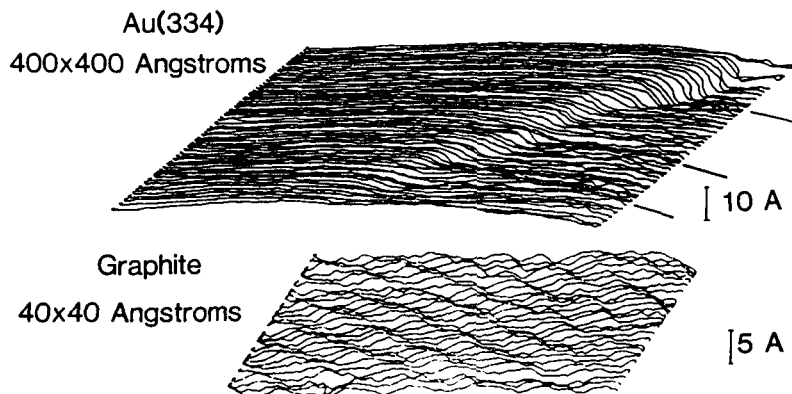


Figure 6.
Scanning Tunneling Microscope
images in air.

of epitaxial overlayers of metals and oxides on semiconductor and metallic substrates, to investigate adsorbate covered model catalyst surfaces and explore the applicability of this technique to solid liquid interfaces.

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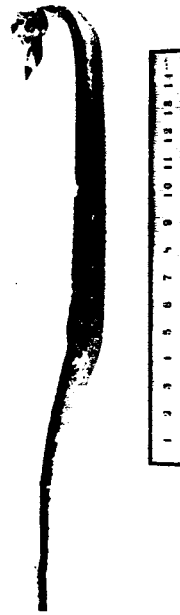
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Note:

Invited or Contributed Papers which subsequently appeared as Publications (refereed) or Other Publications (non-refereed) are listed in both applicable categories.



ELECTRONIC MATERIALS _____

ELECTRONIC MATERIALS

The Electronic Materials Program (EMP) focuses on solving major scientific problems impeding the development of large-scale digital integrated circuits and optoelectronic devices based on gallium arsenide (GaAs). The interdisciplinary basic research effort will elucidate the mechanisms of structural defect formation (e.g. dislocations, point defects, etc.) and impurity distribution during bulk crystal growth, the relationship between the structure and electronic properties of interfaces and the effects of substrate defects on the quality of epitaxial thin films and direct implantation devices.

The Electronic Materials Program relies on close collaboration between scientists dedicated to crystal growth and those with a major interest in materials characterization. The goal of this strong coupling between materials synthesis and analysis is to gain understanding of the complicated relationships which exist between the bulk crystal growth conditions and the structural and electronic properties of the crystals. There are four main areas of GaAs research composing the core part of the program:

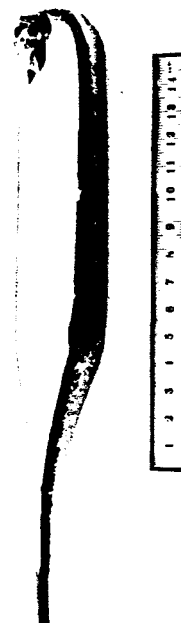
- Development of bulk GaAs growth techniques with precisely controlled growth parameters.
- Studies of correlations between the crystal growth conditions and structural characteristics such as: hardness, dislocation densities, precipitates, etc.
- Studies of the microscopic identity and spatial distribution of major defects responsible for electrical and optical properties of GaAs crystals.
- Structural and electrical investigations of physical and chemical processes occurring at the metal-GaAs interfaces.

Major recent accomplishments of the program include:

- Reproducible growth of 2" diameter single crystals with low dislocation densities.
- Development of a model of As-rich precipitate formation based on extensive electron microscopy studies of pure and doped GaAs.
- Comprehensive studies of the effects of solid phase reactions on the electrical properties of thermally annealed metal-GaAs contacts.

CRYSTAL GROWTH

At present the main effort in the crystal growth area is directed towards studies of new bulk GaAs growth techniques using Electro-Dynamic Gradient Horizontal Bridgman (EDG



HB) furnaces. A major accomplishment in this area was implementation of the technique to grow large diameter (2") low dislocation density (less than 10^4cm^{-2}) single crystals. Extensive studies of thermal profiles in the growth furnaces and their relationship to the shape of solid-liquid interface during the growth allowed the optimization of growth conditions for crystals with specific properties. Studies of the effects of arsenic pressure during the growth on electrical (resistivity) and structural (dislocation density) properties are currently underway. In Figure 1, a 5" furnace is shown. The computer control of the thermal profiles provides good reproducibility of the growth cycles. A single crystal grown in EMP is shown in Figure 2.

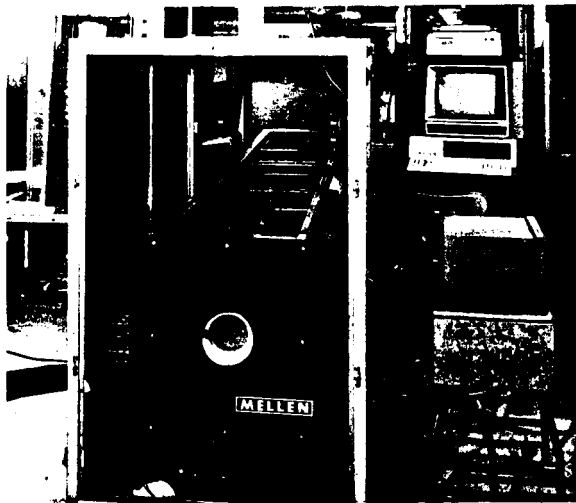


Figure 1.
The 5" PC controlled Electrodynamic Gradient Horizontal Bridgman Furnace.

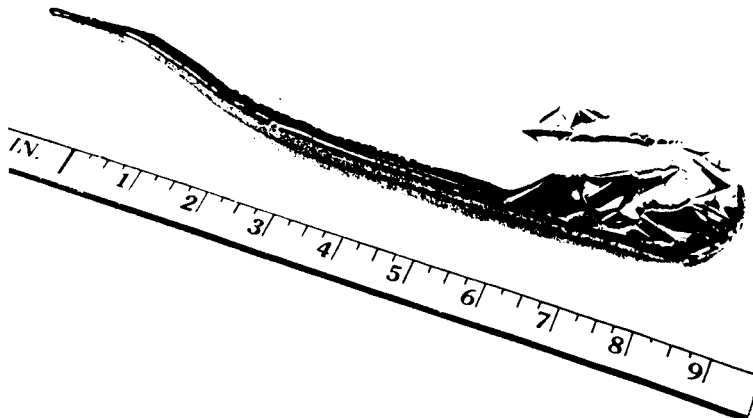


Figure 2.
Single GaAs crystal grown using the EDG HB technique. The tang end of the crystal was quenched to reveal the solid-liquid interface shape.

STRUCTURAL CHARACTERIZATION

Concurrently with the development of EDG HB growth, comparative studies of the crystals grown by different techniques were conducted. In collaboration with Hewlett-Packard Optoelectronic Division, systematic investigations of mechanical properties of undoped and heavily doped GaAs were carried out. An experimental set-up for deformation studies has been modified for high temperature operation. Results of the temperature dependence of critically resolved shear stress (CRSS), i.e. the stress at which dislocation starts to propagate are shown in Figure 3. Contrary to common belief these data show that at high temperatures CRSS does not vary substantially with doping. Our findings have very important consequences for the understanding of the mechanism of dislocation suppression observed in heavily doped GaAs crystals. In particular it proves that the alloy hardening which has been frequently used to explain changes of mechanical properties of alloys is not a main mechanism for dislocation suppression in indium or silicon doped GaAs. Also, the deformation studies provided valuable information on the optimization of the doping strategy for dislocation reduction in undoped semi-insulating and heavily doped n-type GaAs.

The large variety of non-stoichiometry related native defects affecting structural and electrical properties of compound semiconductors is a major impediment in the development of the growth techniques providing materials with well controlled properties satisfying device application requirements. In the case of GaAs, defects related to excess

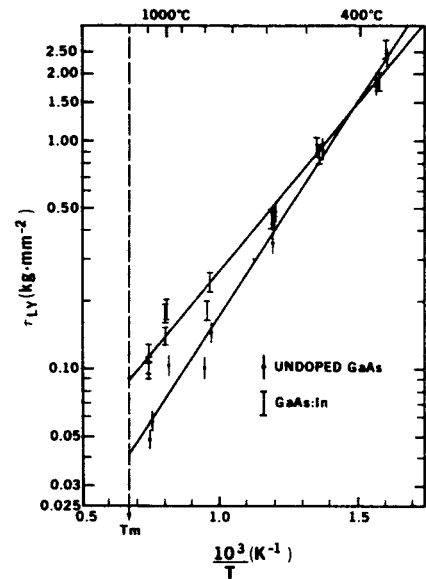


Figure 3.
Inverse temperature dependence of the lower yield stress (or CRSS) for undoped (○) and In-doped (●).

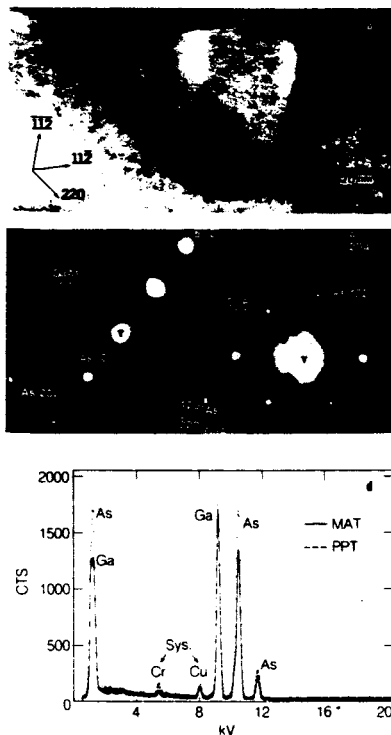


Figure 4.
(a) Multibeam image of a typical precipitate found in In-doped GaAs; (b) and (c) selected area diffraction patterns (SADP) with extra spots indicated; and (d) Results of chemical analysis by energy dispersive x-ray spectroscopy (EDXS). Excess arsenic in the precipitate (PPT) compared with GaAs matrix (MAT) is clearly visible.

arsenic play the most important role. We have undertaken extensive studies of structural and electrical characteristics of such defects. Atomic resolution electron microscopy was used for systematic studies of arsenic rich precipitates in undoped and indium doped GaAs. Sizes of the precipitates were found to range from a few hundred Å to ~ 2000 Å. Their concentration has been estimated to be of the order of 10^8 cm^{-3} . A very significant difference between the precipitates in indium doped and undoped GaAs has been found. As is shown in Figure 4, the arsenic rich precipitates in indium doped GaAs have a characteristic tetrahedral shape reflecting the symmetry of the host crystal. This indicates that there is a strong effect of indium doping on interfacial energies and/or the mechanism of precipitate formation.

ELECTRONIC CHARACTERIZATION

The existence of the arsenic rich extended defects implies that the point defects related to excess arsenic should also be present in significant concentrations. Although these electrically active defects are not detectable with electron microscopy techniques, they play a very important role for the mechanism of electrical compensation in semi-insulating GaAs. Identification of the parameter affecting incorporation of the native defects and finding means to control their concentration during the growth and post-growth cooling is of paramount importance for GaAs technology. Studies of native defects and impurities determining the compensation mechanism in bulk grown GaAs crystals were carried out. Due to the complex nature of the problem, results of various experimental techniques have to be combined for a meaningful characterization of the material. Techniques such as Electron Paramagnetic Resonance (EPR), which is sensitive to microscopic properties of the specific defect, provide means to identify the defect structure whereas macroscopic methods like optical absorption in near and far infrared spectral ranges and electrical measurements are used to evaluate defect concentration and their distribution in large diameter crystals.

The Electronic Materials Program had a number of accomplishments in this area. Thus, measurements of the microwave power dependence of EPR spectra intensity presented in Figure 5 have shown that the main deep donor (EL2), responsible for the semi-insulating behavior of undoped GaAs, is a complex defect rather than an isolated antisite defect (As_{Ga}). Also, a new defect with a very characteristic EPR spectrum has been discovered. The role of this defect in the compensation mechanism is currently being studied.

The impurity which is believed to be critical for semi-insulating behavior of GaAs is carbon. The information about the spatial distribution of carbon in large diameter crystals is essential for understanding the origin of macroscopic inhomogeneities of electrical and optical properties. In

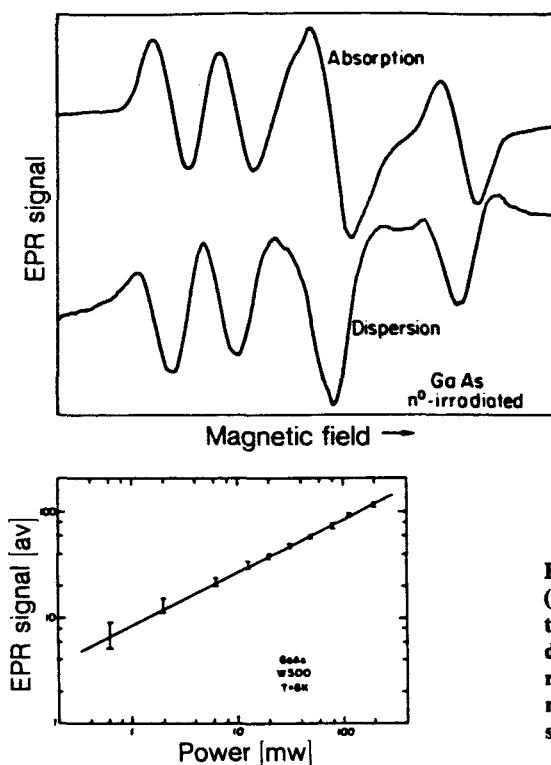


Figure 5.
(a) Quadruplet related to arsenic antisite defect measured in the absorption and dispersion mode. (b) Microwave power dependence of EPR signal measured in the absorption mode. Linear dependence of the intensity up to the highest microwave power indicates a complex nature of the defect strongly interacting with the crystal lattice.

cooperation with M/A Com Advanced Semiconductor Systems, a new method for determining the distribution of shallow carbon acceptor and compensating donors has been developed. The method is based on an analysis of the local vibration mode (LVM) spectra. The difference between LVM spectra for ionized and for neutral carbon acceptors is employed for the evaluation of the degree of compensation of the carbon acceptor after optical quenching of the major deep donor (EL2). Measurements carried out on 2" diameter crystals are shown in Figure 6(a) and (b). The most significant result deduced from these measurements is that the compensating donors are inhomogeneously distributed. We have shown for the first time that their concentration exhibits a characteristic "W"-shape across the wafer. This finding brings a new understanding to the origin of the very well known W-like distribution of the ($\sim 1 \mu\text{m}$) optical absorption in the near infrared. This absorption was typically interpreted as the measure of the EL2 concentration. Our data show that even if EL2 is homogeneously distributed in the wafer, spatial variations of absorption of GaAs wafers will be induced by a nonuniform distribution of donors with energy levels shallower than EL2.

The progress in GaAs device technology depends not only on the quality of the bulk grown crystals but also on the successful development of reliable, stable and reproducible Schottky contacts. This is especially true for metal-semiconductor field effect transistor (MES FET) technology, where good metal-semiconductor contacts are essential for proper device operation.

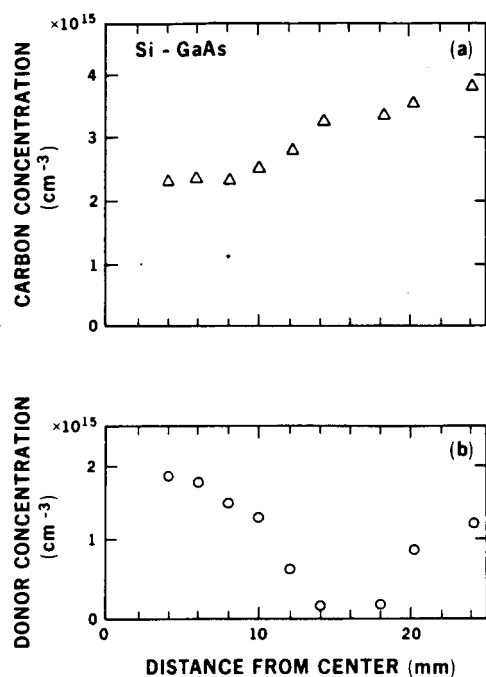


Figure 6. (a) Spatial distribution of carbon concentration in 2" diameter semi-insulating GaAs crystal; (b) Distribution of the concentration of compensating donor defects deduced from the variation of the shape of LVM spectra.

Detailed studies of structural and electrical properties of metal-GaAs contacts have been conducted in the past year. A large variety of metals with different chemical and physical properties have been used for this study. Special attention was paid to refractory metals because of their high thermal stability. A number of experimental techniques have been used including atomic resolution transmission microscopy and heavy ion Rutherford backscattering (HIRBS). The structural changes of the metal GaAs interface have been correlated with changes of electrical characteristics of the Schottky contacts. Effects of annealing at different temperatures were studied to identify the most stable metal-GaAs systems and to reveal chemical reactions leading to deterioration of the Schottky barrier. Figure 7 shows an example of HIRBS

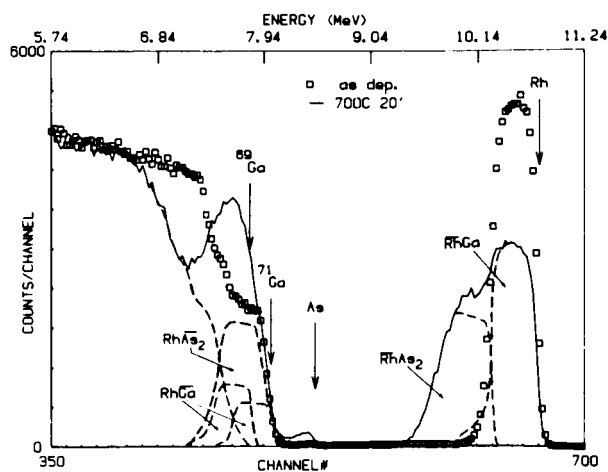


Figure 7. Heavy ion RBS of the Rh-GaAs system with 20 MeV ¹⁶O projectiles. Various chemical phases formed during the deposition and after 700C annealing are indicated.

spectra taken on the Pd-GaAs system. A very important accomplishment in this area was the development of a new mechanism for the GaAs Schottky barrier formation. The mechanism is based on the existence of amphoteric native defect systems in GaAs. The identity (acceptor or donor) of such systems is determined by the relative position of the Fermi energy in respect to the defect energy levels in the band gap. The mechanism provides the explanation for the Fermi level pinning energy for low metal coverages and, as is shown in Figure 8, correctly predicts the dependence of the Schottky barrier heights in n- and p-type GaAs on the metal electronegativity.

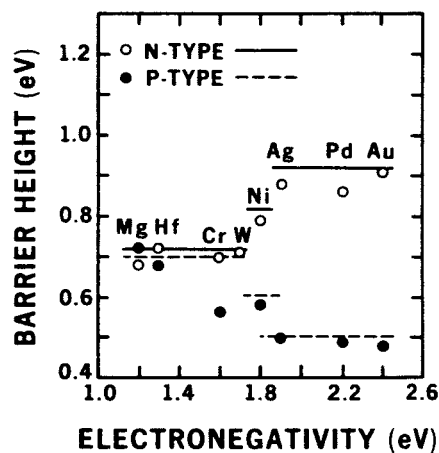


Figure 8.
Predicted trends for metal electronegativity dependence of Schottky barrier heights on n- (solid line) and p-type (dashed line) GaAs.

During the last year, research in EMP was consolidated around a few issues critical for GaAs technology. A new growth technique has been developed to the point that good quality GaAs single crystals can be reproducibly grown. A number of advanced characterization techniques have been used to develop new methods for the assessment of properties of GaAs crystals.

New significant results illuminating the role of native defects in the determination of electrical and structural properties of bulk GaAs and metal-GaAs interfaces have been obtained. These results provided feedback for improvements of the crystal growth technology. In the near future the major findings obtained from the horizontal EDG growth experiments will be used for development of crystal growth in a vertical configuration.

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Note:

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CERAMIC AND METAL INTERFACES

CERAMIC AND METAL INTERFACES

The servicability of many structural and electrical components and assemblies hinges on good ceramic-metal bonding where failure of the interface will lead to loss of electrical continuity, protection against wear or corrosion, or other service function. Thus, development of a mechanical theory of adherence between dissimilar materials and demonstration of the metallurgical principles to achieve superior resistance to decohesion are the primary goals of this program.

Most studies of adhesion are based on chemistry disciplines of contact angles, wetting, and interfacial energies. These parameters are important and occasionally dominant, but, in general, other irreversible surface and bulk processes are equally important. The performance and reliability for a myriad of technological applications, such as multilayer electronic components, are limited by interfacial fracture, after fabrication. Thus, a fracture mechanics perspective is more appropriate than simply a binding force or surface energy analysis.

Elucidating fundamentals of decohesion requires attention to interfacial bonding, to crack tip deformation, and to crack interactions with interface morphology and reaction phases. During the past year major constituents of the fracture energy of ceramic-metal interfaces were identified, and ensuing interrelations between interfacial chemistry, local plasticity, and microstructural crack shielding demonstrated.

Parallel analyses of recognized problems of industrial relevance treat decohesion of particular deposited and reaction-formed films which, respectively, have high tensile and compressive residual stresses. These studies reveal the additional need for attention to specific geometries, stress concentrations, and internal stresses. Decohesion modes have been determined for both cases and theories for growth stresses developed for the latter. A key aspect that emerges is the tendency to delaminate in response to the growth stresses when films attain a critical thickness.

The program currently has four primary foci:

- Ceramic-Metal Interfacial Fracture Energies
- Internal Stress-Induced Film Delamination
- Delamination of Reactively Formed Coatings
- Indentation-Induced Film Delamination



CERAMIC-METAL INTERFACIAL FRACTURE ENERGIES

The mechanical failure of ceramic-metal couples due to applied and residual stresses as modified by edges, plasticity or discontinuous elastic moduli is often quite brittle, and so the strength is determined by the fracture toughness at or near the interface and by the flaws that initiate fracture. Thus, interfacial fracture energy, G_c , is a fundamental and useful measure of adhesion, although few prior assessments of it exist. Current estimates for the magnitude of and interrelationships among components of the interfacial toughness already provide useful guidance for designing improved devices.

The direct influence of interfacial chemistry and structure on the resistance to interfacial fracture, Figure 1, is reflected by the work of adhesion, W_{ad} , i.e. the equilibrium energy balance for the surfaces destroyed and the interface created. However, irreversible losses during bond breaking at the tip and formation of metastable surfaces (in the absence of diffusional reconstruction), as well as plasticity, can also significantly impede fracture.

Fracture of brittle oxides reveals aspects of the nonplastic, but poorly understood dissipation during bond scission which is reflected by the ratio, ξ , of fracture energy to $(-W_{ad})$. Prior evaluation here of single crystal cleavage indicated $\xi = 1-3$ or more with lower values for fracture surfaces having denser atom packing. Work on Al_2O_3 shows that grain boundary fracture is predominate for subcritical crack growth, whereas rapid extension is primarily transgranular. Evidently the irreversibilities for boundary fracture are appreciable (as $-W_{ad}$ for boundaries is about half that for crystals) and are effectively reduced by thermal activation. Similarly the interfaces are more susceptible to moisture assisted crack growth, which typically controls at room temperature.

Further toughening from plasticity depends upon the metal yield stress and local resistance to interfacial cleavage. Simple models show limiting regimes of nearly brittle and ductile behavior exist which have opposite influences of the yield stress on toughness, Figure 2. A high yield stress confines deformation to a small zone and limits crack tip blunting, Figure 1. In ductile regimes, the toughness and crack geometry are not unique, but depend upon specific constraints on the amount of plasticity during crack advance. Under specific conditions, the fracture energy is proportional to the yield stress and film thickness.

The interfacial fracture energies from DCB tests of glass bonded with Cu films, Figure 3, are distributed within 0.14 to 8 J/m² owing to differing yield stress, Cu thickness, extent that fracture remains at one interface, and especially interfacial chemistry. The latter is largely dictated by methods of cleaning the glass and diffusion bonding the Cu, and

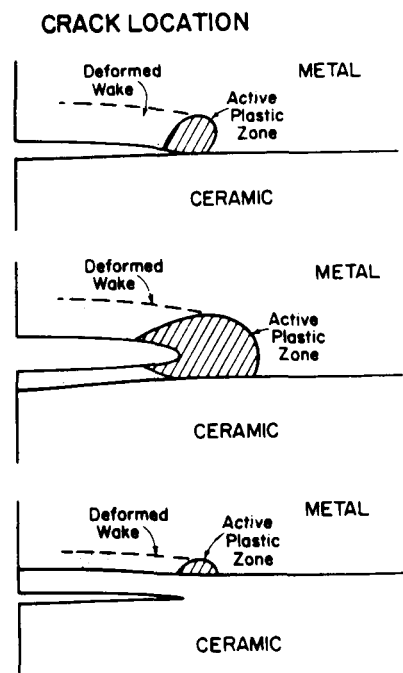


Figure 1.
The crack location and amount of plastic work accompanying propagation determine the fracture energy.

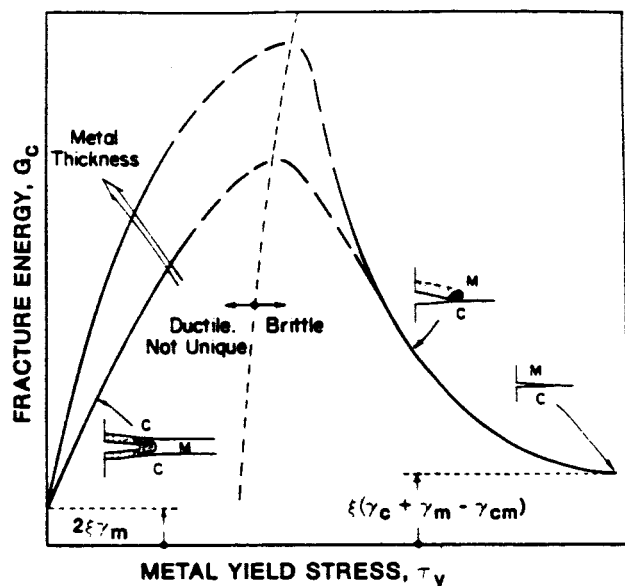


Figure 2. Expected dependence of fracture energy on metal yield stress. At higher yield stress, cracks extend along the interface; the near tip plastic zone and work increase with bond rupture resistance at the tip and diminishing flow stress. At lower yield stress, cracks blunt and may extend through the metal; the dependence on yield stress is opposite.

seemingly by stress corrosion from the ambient test atmosphere. The highest toughness, derived from samples provided by IBM-Almaden which were ion etched prior to Cu deposition, is similar to that for glass. A 10–20 nm Cr underlayer improves chemical bonding, often raises G_c , and imparts a greater tendency to crack the glass.

Two distinct deformation modes operate during fracture, as established by optical and electron microscopy of the Cu. The near crack tip plasticity is manifest by a higher dislocation density near the cracked interface. The density decreases from above 10^{11} to 10^9 cm^{-2} within the first micron for a tougher sample, but is much smaller, indicating less plastic work obtains, in contaminated samples with poor interfacial bonding.

Various modes of local decohesion at a second interface permitting the Cu film to be stretched during fracture, Figure 4, can impart greater toughness. This combination of crack tip shielding by out-of-plane microcracking and bridging behind the crack tip should be applicable in toughening multilayer devices or ceramic-metal seals.

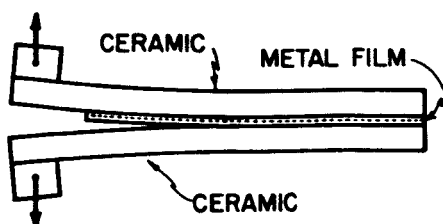


Figure 3. The double cantilever beam (DCB) technique used to measure fracture resistance with bonded pairs of metal films previously deposited onto ceramic substrates.

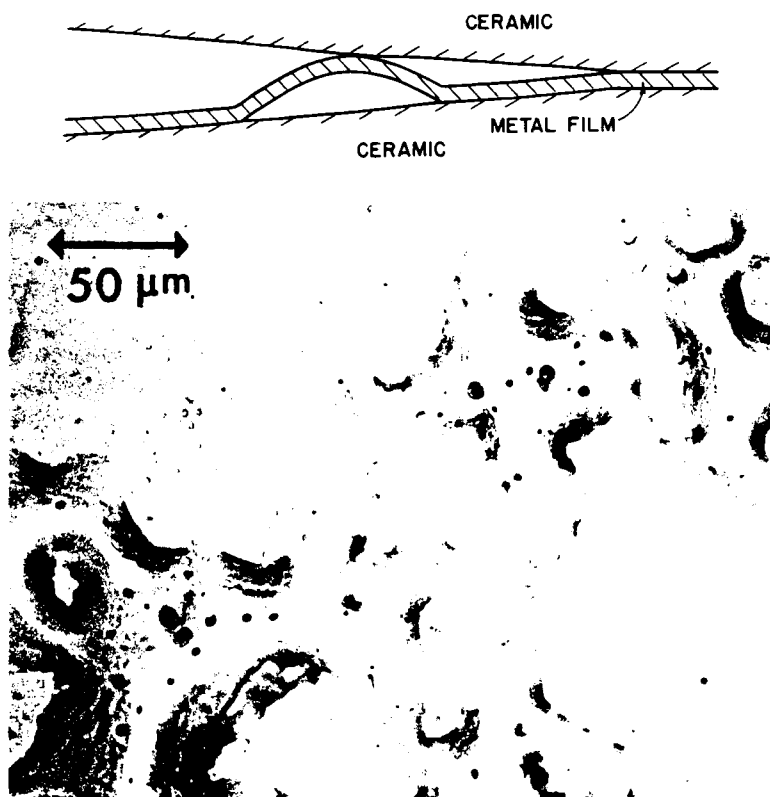


Figure 4. Bridging bulges formed on the primary fracture surface result from decohesion at a parallel interface and stretching of the Cu film as the primary crack passes. The extra deformation and fracture area can more than double the fracture energy.

INTERNAL STRESS-INDUCED FILM DELAMINATION

Spontaneous delamination of well-bonded films from substrates can result from large residual growth or thermal mismatch stresses in the film itself. The potential for loss of protection or other device failures is exacerbated by stress concentrations at film edges and mechanical or chemical damage during service. Fracture mechanics based relationships between key variables along with baseline values for materials parameters provide useful insight into the susceptibility to delamination observed under very large tensile or compressive growth stresses.

The parameter $\sigma_r^2 t / EG_c$ describes decohesion susceptibility due to residual film stresses, σ_r . The delamination driving force approaches a value, $f(v)\sigma_r^2 t / E$ that depends upon crack geometry, but is nearly insensitive to crack sizes that significantly exceed the film thickness, t . Thus, below a critical thickness, spontaneous delamination cannot occur, despite the presence of large flaws.

Striking examples of splitting and delamination of low temperature vapour- or electro-deposited chromium films

induced by inherent tensile stresses, have been studied, in part, using films deposited by IBM-Almaden. For vapour-deposited Cr, high interfacial toughness permits local shear stresses to induce a transition from interfacial to substrate delamination, 1 to 3 film thicknesses deep, that occurs more readily for Si than for tougher glass substrates, Figure 5. Atmospheric moisture enhances delamination for Cr/glass, but seemingly not for Cr/Si. Low temperature annealing exacerbates decohesion evidently by *increasing* residual stresses. With some deposition conditions, the ensuing profuse, fine microcracking limits stresses and prevents gross splitting and delamination.

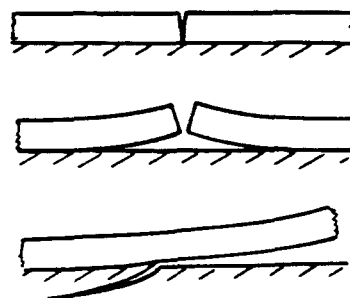


Figure 5. Spontaneous splitting, delamination and curling of vapour-deposited 1.1 μm Cr films from sputter-etched glass substrates induced by large residual tension. The films first split along lines radiating from the evaporation source. Subsequently, long ribbons crack across, delaminate, and curl, in part, from stress gradients through the film. Initially, cracks extend from the splits at or near the interface, but final delamination often occurs within the substrate.

Reaction-formed oxide coatings often fail by buckling, delamination, and spalling induced by high compressive stresses. In severe cases, recurrent cycles lead to damage beyond servability. Present treatments of the intertwined growth mechanisms, stresses and morphology, and of mechanisms for pore or crack formation at the interface or within the oxide, have broad applicability, e.g. to silicide films.

New perspectives on delamination and exfoliation of protective coatings resulted from recent work on Cu. Thermal cycling or isothermal heating caused unexpectedly rapid oxidation of electrodeposited or vapour-deposited copper. Unusually fine buckling and spalling of the oxide films also obtained at temperatures as low as 160°C, when the oxide achieved a *critical thickness*, about 0.3 microns.

DELAMINATION OF REACTIVELY FORMED COATINGS

Various morphologies formed, but most frequent was a sinusoidal wormy growth of delaminated and buckled regions; these intergrow giving multiple buckling, occasionally coalesce, and eventually lead to spalling, Figure 6. These effects appear to stem primarily from the very fine grains and high defect content within the oxide which presumably derive from the deposited copper.

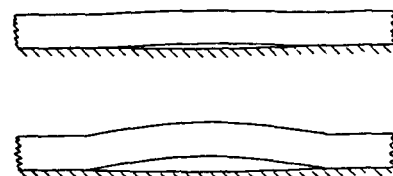


Figure 6. Microbuckling and spalling of oxide formed on electroplated Cu at 200°C in response to high growth stresses, perhaps augmented by mismatch stresses from thermal cycling, tend to occur when scales attain a critical thickness. The problem was first manifest during an investigation of Si solar cells from PG&E Research Facility, San Ramon, California.

A two dimensional model developed for forming oxide with columnar grains by boundary diffusion, in combination with prior theory developed here for oxidation by volume diffusion, permits prediction of the large stresses usually generated during oxidation and of microstructures that prevent them. The stresses depend upon the relative diffusion rates of metal ions out of and oxygen in through the oxide, the dominant diffusion paths, the relative molar volumes of the oxide and metal, and the morphology of the oxide scale and base material. If fine columnar grains in the oxide allow boundary diffusion of oxygen to accelerate oxidation of the copper, very high ($\sim 0.02E$) compressive stresses are predicted, which would drive buckling.

A preliminary mechanics evaluation, in concert with the oxidation theories, explains several aspects of the buckling. At the observed critical thickness and larger than minimum buckle sizes (needed to stabilize buckling) the driving force for the requisite decohesion, predicted using published theory for single buckles, approaches 5 J/m^2 , a plausible value for semi-stable oxide buckles on copper. However, the multiple buckling patterns and the flaw population that permits buckling to initiate are only partially understood. Impurity accumulation at the interfaces may reduce the fracture

energies sufficiently to allow pore formation in response to predicted stresses normal to the interface and coalescence into a crack.

INDENTATION-INDUCED FILM DELAMINATION

Indentation methods which induce film delamination are applicable for estimating G_c as well as modelling contact damage to films.

Indentation tests on 8 μm sputtered ZnO and 0.5–1 μm evaporated Cr films on glass show that decohesion increases with penetration depth, d , even if it far exceeds the film thickness until nonuniform film buckling and cracking limit the delamination when d/t exceeds 4–10. Apparently, determination of G_c can be extended to a wider thickness range than had been expected (with improved analysis). Interfacial delamination of Cr films was very sensitive to variations in substrate cleaning; preliminary analysis indicates that G_c varied by 1 to 2 orders of magnitude.

Additional studies involving wetting, adhesion, and thin film microstructures were funded by NASA and NSF. New approaches to waterproofing Space Shuttle tiles based on effects of thermal processing and coatings on the contact angle of water with silica fibers have evolved. The composition and microstructure dependence of plasma-activated CVD films of amorphous SiC:H on the silane/methane ratio and substrate type and temperature were determined by analytical TEM. These films were found to be very adherent to glass and Al; those with higher carbon (C/Si > 1) were virtually hydrophobic, in contrast to crystalline SiC.

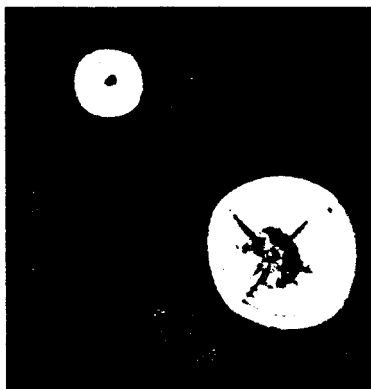
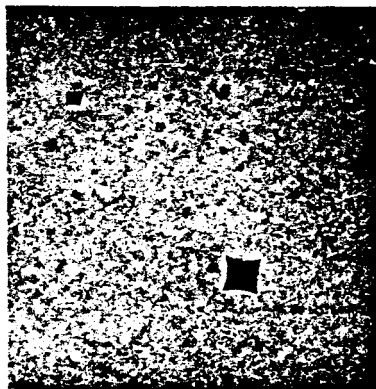
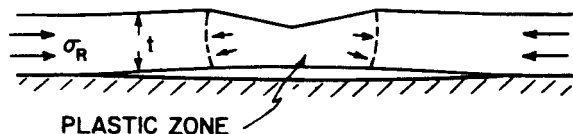


Figure 7.
Indentation-induced film delamination for ZnO on glass; viewing from below better reveals interfacial delamination.

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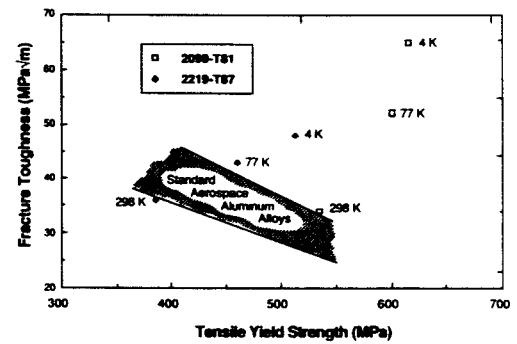
- Fisher, R.M., *The Critical Voltage Effect in Metals, Alloys and Compounds*, Beijing Conference and Exhibition on Instrumental Analysis, Beijing, China, November 1985. (Proc. 1st Beijing Conference and Exhibition on Instrumental Analysis, vol. 1, p. 232, 1987.)

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- Fisher, R.M., *Computation of the Hardness of Carbon Steels*, 114th Annual Meeting of the American Institute of Mining and Metallurgical Engineers, New York, New York, February 1985.
- Fisher, R.M., B. Martin, and R.M. Cannon, *Low Temperature Oxidation and Spalling of Electrodeposited and Vapour-Deposited Copper*, Meeting of the Materials Research Society, Boston, Massachusetts, December 1985. (Mat. Res. Soc. Proc., vol. 54, p. 829, 1986)
- Fisher, R.M., B. Martin, R.C. Dobbyn, M. Kuriyama, and D.R. Black, *X-Ray Topography of Silicon Solar Cells and Thin Metal Films*, Meeting of the Materials Research Society, San Francisco, California, April 1985.
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Note:

Invited or Contributed Papers which subsequently appeared as Publications (refereed) or Other Publications (non-refereed) are listed in both applicable categories.



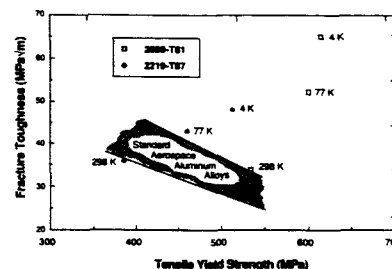
STRUCTURAL MATERIALS

STRUCTURAL MATERIALS

The Structural Materials Program in the Center for Advanced Materials is intended to apply recent progress in the fundamentals of materials science to the solution of generic materials problems that affect American industry. The current research in areas in the development and performance of four engineering materials that were selected after consultation with the Department of Energy and concerned industries are:

- Light alloys for advanced aerospace systems
- Sheet metal forming for advanced manufacturing
- Fatigue-resistant solder joints for electrical contacts
- Advanced superconductors and cryogenic structural materials for magnetic fusion energy devices

Each of these research programs is conducted in collaboration with industrial or national laboratory groups that are potential users of the research and receives supplementary funding from industry or from offices of DOE in addition to the Division of Materials Sciences. Research on light alloys is done in collaboration with several aluminum and aerospace companies, and receives supplementary funding from Aluminum Company of America (Alcoa) and the Lockheed Corporation. Research on sheet metal forming is done in collaboration with General Motors and the Los Alamos National Laboratory and receives supplementary funding from GM. Research on solder compounds is done in collaboration with several electronics companies and has received funding from Western Digital and from Boeing Aerospace. Research on materials for high field superconducting magnets is done in collaboration with the Lawrence Livermore Laboratory and receives funding from that Laboratory. Its Department of Energy funding is from the Office of Magnetic Fusion Energy.



LIGHT ALLOYS FOR ADVANCED NEW SYSTEMS

The current focus of the light alloys program is on aluminum-lithium alloys for aerospace applications. These alloys have been formulated as a result of a concentrated research and development effort over the past decade both here and abroad aimed primarily at the commercial aircraft market. The lithium-containing alloys help to reduce aircraft weight by providing lower densities and higher elastic density than competing aluminum alloys while retaining equivalent or better mechanical properties. However, in many ways aluminum-lithium alloys are strikingly different from current aluminum alloys. In response to suggestions from both the aluminum and the aerospace industries, work in our program has focussed on understanding potential in-service failure

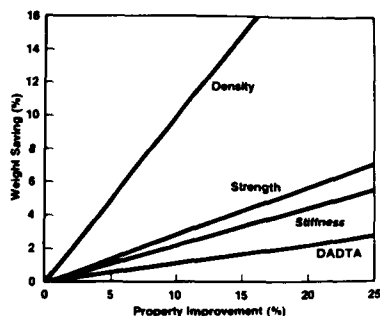


Figure 1.

A primary goal of aircraft designers is to improve the payload capacity and/or fuel efficiency of the aircraft by lowering its structural weight. The graph at left illustrates the results of a typical design study on the effects of improving material properties on the structural weight. Lowering the density of the structural materials while retaining other properties at the same level is considerably more effective than improving their strength, elastic stiffness or fatigue, fracture and corrosion resistance (DADTA). Alloying aluminum with lithium lowers the density of the material, making aluminum-lithium alloys an attractive material choice. Recent metallurgical advances make it possible to achieve these lower densities without sacrificing other mechanical properties.

modes (for instance due to corrosion or fatigue) and on exploiting unique properties of these alloys for specialized applications (for example at extreme temperatures).

Most of this work has concentrated on a high-strength commercial alloy, 2090-T81. The program was highlighted by the finding that this alloy has dramatically improved strength and fracture toughness at 4 K. This work has helped to spur serious consideration of aluminum-lithium alloys for cryogenic fuel tanks for proposed space vehicles.

Cryogenic Mechanical Properties

The principal application of aluminum alloys at cryogenic temperature is for large tanks used to hold cryogenic fuel (e.g., liquid hydrogen or oxygen) to power space vehicles ranging from the space shuttle to the proposed hypersonic and transatmospheric vehicles. Interest in aluminum-lithium alloys is high because space vehicles are highly weight-critical. LBL expertise and facilities for cryogenic mechanical properties evaluation make this an obvious area in which CAM can make a unique research contribution. CAM research in this area has focussed on measuring some key engineering properties of 2090-T81 for this type of application and on initial studies of the mechanisms responsible for the exceptional properties we measured.

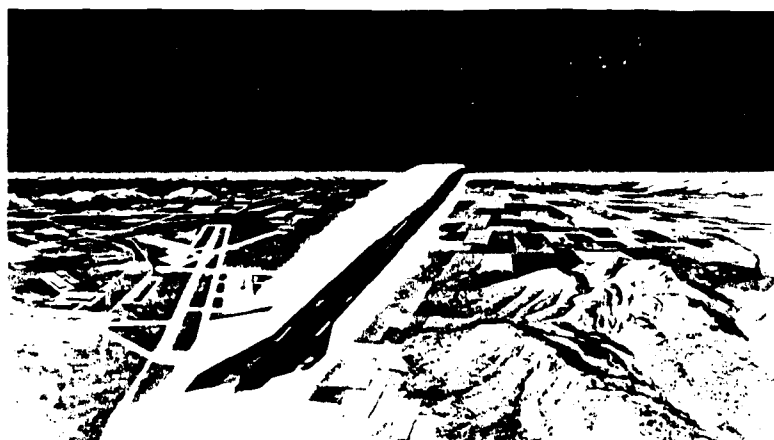


Figure 2.

The newest aerospace initiatives are for hypersonic and trans-atmospheric vehicles. These vehicles include the proposed National Aerospace Plane (NASP), pictured at left, which is projected to cross the Pacific in less than two hours. All of these designs assume cryogenic propellants that will be contained in large, structural tanks. Aluminum alloys are strong candidates for this application. Because of their light weight and good low temperature properties the feasibility of constructing these tanks from aluminum-lithium alloys is being investigated. (Photo courtesy of Lockheed Corporation.)

Tests conducted at LBL and at Lawrence Livermore National Laboratory showed that the yield strength, ultimate tensile strength, fracture toughness and elongation of 2090-T81 all improved as temperature decreased. Consequently, the strength-toughness combination (the most important design parameter) improves dramatically as temperature decreases. At the lowest temperatures, 4 K, 2090-T81 is far superior to any aluminum alloy currently used for cryogenic applications (Figure 3). A study of underlying microstructural basis of the low temperature properties has been initiated under a grant from the Aluminum Company of America (Alcoa).

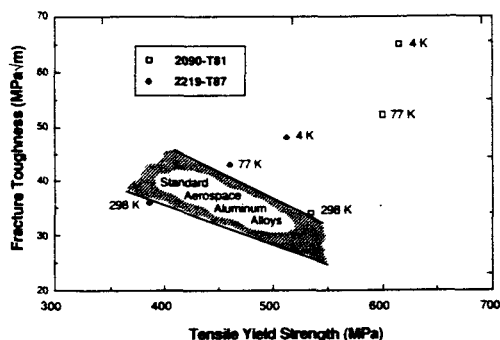


Figure 3.

Aluminum-lithium alloy 2090-T81 has superior properties to any existing aluminum alloy at cryogenic temperatures. The diagram at left compares combinations of yield strength and fracture toughness for aluminum alloys. The hatched band indicates the range of properties at room temperature for conventional alloys. At room temperature, the combination of properties obtained for 2090-T81 is among the highest. At lower temperatures the properties of 2090 improve dramatically. Properties of 2219-T87, the aluminum alloy most commonly used for cryogenic applications today, are shown for comparison.

A specialized requirement for tankage is an alloy that can be welded in large sections. In collaboration with Lockheed-California Corporation, we have also initiated weldability studies of 2090 sheet. The results suggest that with appropriate post-weld processing, acceptable properties can be achieved.



Figure 4.

These photographs are scanning electron micrographs of the fracture surfaces of 2090-T81 broken at three temperatures, 298K, 77K and 4K. Although the fracture toughness measured when these specimens were broken increases significantly at low temperatures, the fracture mechanism is unchanged. Work is now underway to investigate changes in the deformation behavior of the material at low temperatures.

Reliability

Although the newly commercial aluminum-lithium alloys have been tailored to have similar design properties in an engineering sense, the mechanisms responsible for those properties appear to be significantly different than those operative in older alloys. Because these alloys have moved from initial research to application so rapidly, there is a concern within the industry that time-dependent properties such as fatigue and corrosion resistance are not sufficiently

well understood for safe use. These concerns center around the problem of identifying accelerated tests that correlate with in-service exposure. Until the mechanisms underlying fatigue and corrosion behavior are understood, there is no guarantee that existing tests will correlate well with actual behavior.

A series of investigations were planned after extensive consultation with both civilian and military aircraft manufacturers. Our findings indicate that the fatigue properties of 2090 are superior to those of existing alloys at moderate load cycles, both at room temperature and at low temperatures. However, fatigue cracks are accelerated by compression overloads to a much greater degree. Cracks that are microstructurally short also grow at more accelerated rates in these alloys than in conventional alloys.

Additional fundamental work in support of the industrially oriented program described above, focuses on the theory of strengthening of alloys hardened by the ordered precipitates found in aluminum-lithium alloys. This work leads to both qualitative and quantitative predictions about the strength of simple alloys. Experimental work on binary aluminum-lithium alloys is also being conducted in support of each of the projects described above.

In support of the nation's major producers and consumers of sheet metal and sheet metal products, this program is undertaking a fundamental investigation into sheet metal formability. While the types of formable materials and their applications are varied, the main thrust of the effort is geared toward determining the possibility and direction of improved formability of low carbon steel for use in the automobile industry. Here, where low material cost is the primary factor in material selection, improved formability may permit the use of thinner sheet which can lead to both material savings and lighter, more fuel efficient vehicles. On this program we are collaborating with researchers at both General Motors (GM) and the forming research group at the Los Alamos National Laboratory (LANL)

The limiting problem in sheet metal formability is not one of fracture, but rather one of plastic instability. This can be viewed as the point at which the competition between the geometric softening (which is due to a reduction in load bearing cross section during tensile elongation) and material strengthening via work hardening (which is due to interaction of the dislocations responsible for deformation) is won by the geometric softening.

Consideration of a typical engineering stress-strain curve for low carbon steel in uniaxial tension (Figure 5) reveals that this competition, rather than being won by the geometric softening, is actually lost by the work hardening. The rate of work hardening, which roughly corresponds to the slope of

SHEET METAL FORMING

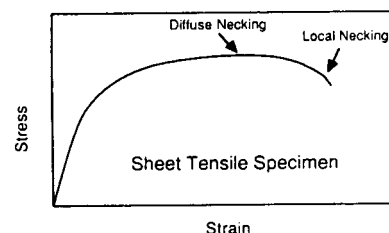


Figure 5. Typical schematic engineering stress-strain curve for a low carbon steel tested in uniaxial tension. The failure criterion for necking instability is given by $d\sigma/d\epsilon = \sigma$, where σ is the true stress and ϵ is the true strain. The work hardening rate (roughly given by the slope of the curve) is very high at low strains and decreases steadily as strain increases. This behavior is the opposite of that which is desired for formability.

the stress-strain curve, is seen to be very high initially, followed by a steady decrease to a very low final level at the point of instability. Since the instability point is theoretically defined as the point at which the slope of the true stress-strain curve equals the true stress, this means that the material behaves in a manner opposite to that which is desired. Ideally, one wishes the work hardening rate to be low at the beginning, where the stress is low, and then to gradually increase, always keeping just ahead of the value of the true stress.

The Formability of Steel

Based on continuing discussions and collaborative meetings with researchers at GM and LANL, our approach has been to attack the problem from both ends. The initial study was to examine the relevance of enhanced geometric softening due to void growth caused by inclusions in the steel, i.e., the relevance of steel cleanliness. The second phase of the investigation, which is currently the main focus of our work, is to investigate the work hardening phenomenon from a mechanistic and behavioral standpoint.

The recently completed work on the effect of steel cleanliness revealed that, at the present inclusion level (about 5×10^{-4} volume fraction), the inclusions were irrelevant to possible improvements in formability for punch stretching operations. Thus further improvements in steel cleanliness should not be pursued, but rather the direction of research should be toward possible improvements in the work hardening characteristics, our second area of research.

Unfortunately before any alloy design work can be done in this area, it is essential to have a complete understanding of the work hardening phenomenon from the standpoint of mechanisms and behavior. Currently that understanding is lacking. One behavioral phenomenon of possible relevance to the work hardening process is the formation of a dislocation cell structure during deformation. While it is known that a dislocation cell structure forms quite early during deformation and is present until failure, its relationship to deformation and work hardening is not yet well understood. In our program one study which has been completed involved the identification for correlations between the predicted active slip systems and the morphology of the dislocation cell structure under various strain states (Figure 6).

Current work involves mechanical testing of materials with different dislocation cell structures to attempt to assess whether cell formation has a positive or negative effect on the subsequent mechanical behavior. To complement these studies, *in situ* tensile experiments using the 1.5 MeV High Voltage Electron Microscope at the National Center for Electron Microscopy at LBL are being carried out to shed light on both the dislocation cell formation mechanism and its relationship to work hardening during deformation of low carbon steel.

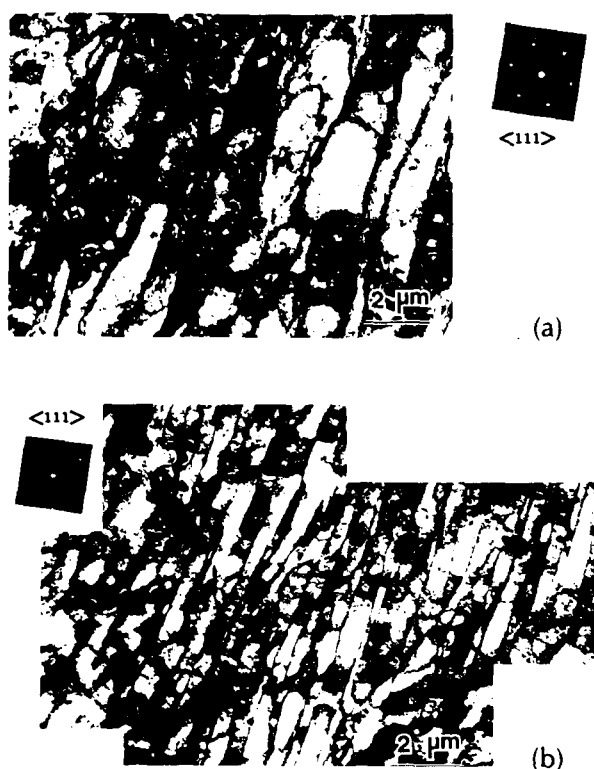


Figure 6.

In-plane transmission electron micrographs of two different dislocation cell structures developed during deformation. a) Positive biaxial stretching produces a diffuse, comparatively equiaxed cell wall structure in which the cell wall traces lie roughly parallel to the predicted active slip planes. b) Uniaxial tension produces an elongated, sharply defined cell wall structure in which there is considerable deviation of the cell wall traces from the predicted active slip planes. These phenomena are currently under investigation.

ELECTRICAL CONTACTS

The advent of high speed computers has brought electronic packaging into the limelight of materials research. Electronic packaging is a method by which electronic components (such as semiconductors) can be housed and isolated from an external environment while allowing electric signals to pass into and out of the component. It is essential that the packages be reliable; the failure of any part of a package could render the entire computer inoperable. An important aspect of the reliability of the electronic package is Pb-Sn solder. The solder is used to join the electronic components to the package, or the package to a printed circuit board while providing mechanical stability for the package and conductivity for the electric signals.

There is a great deal of concern in the industrial community about the failure Pb-Sn solder joints in electronic packages. In service the package undergoes thermal fluctuations that, combined with the different thermal expansion coefficients of the materials used in the package, cause thermal fatigue in the solder joints (Figure 7). The industrial standard for these thermal fluctuations is -55°C to 125°C . Our contacts within the industry (IBM, Western Digital, and Boeing Electronics, among others) have stated that the thermal fatigue problem is important and worthy of additional fundamental research. The goal of this research project is to understand and improve the thermal fatigue

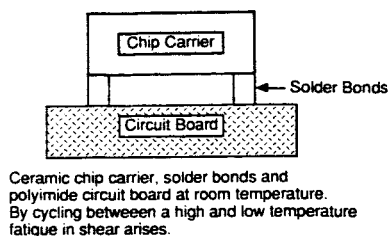
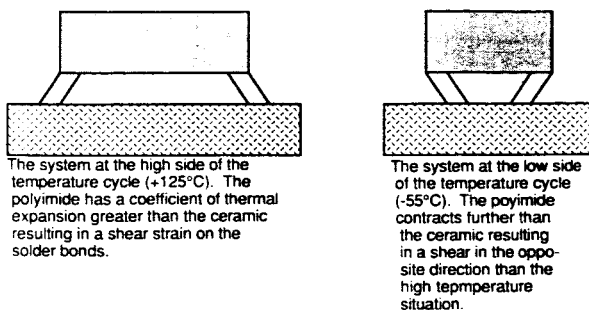


Figure 7.

Origin of thermal fatigue in an electronic package. The Pb-Sn solder is much more ductile than any other material in the package and therefore the solder joints take up all the deformation in fatigue.



properties of solder joints. To reach this goal it is first necessary to examine the microstructure of Pb-Sn solder in a joint configuration and then relate the microstructure to the mechanical properties of the joint (such as strength, toughness, and fatigue resistance of the solder joint to thermally induced strains). The initial microstructure of the solder joints has been characterized by our group and was found to contain interesting intermetallics that have a strong effect on the strength of the joint. Our group has also designed and built computer controlled devices to perform thermal fatigue tests on solder joints.

Microstructure of Solder Joints

The microstructure of the intermetallics that form when 60Sn-40Pb solder is joined to Cu surfaces was investigated. At the interface between the solder and Cu a two-phase intermetallic forms. Adjacent to the Cu a columnar Cu_3Sn phase forms, and adjacent to the solder Cu_6Sn_5 phase forms. Both intermetallics are brittle and preferentially fracture when joints are tested at high strain rates. Intermetallics were also found to form within the solder (Figure 8). The interesting feature of these intermetallics is that they appear as hexagonal tubes of Cu_6Sn_5 intermetallic filled with solder. The hexagonal rods of Cu_6Sn_5 form at the interface and break off into the molten solder. The core of these rods is then etched away in the molten solder leaving tubes. Specimens of 60Sn-40Pb solder containing intermetallic tubes were strained to failure revealing the fracture surface shown in Figure 9. The tubes act as nucleation sites for fracture and are detrimental to the mechanical properties of the solder; in particular the life of the solder in fatigue is decreased with

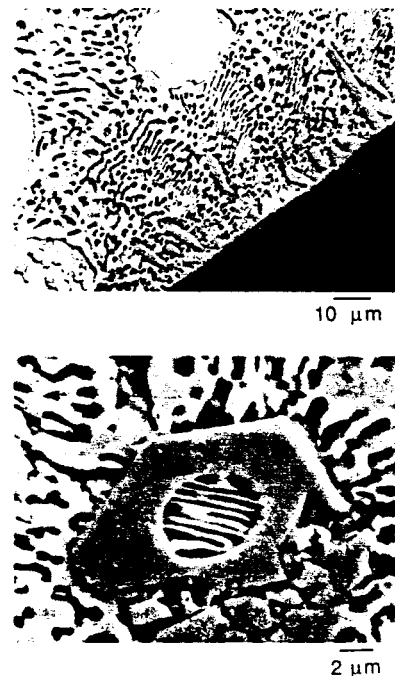


Figure 8.

Scanning electron micrograph of intermetallic precipitates of Cu_6Sn_5 in 60Sn-40Pb solder/Cu joint. These hexagonal rods form at the solder/Cu interface and break off into the molten solder. Within the molten solder the inner portion of the rod is etched away and fills with solder resulting in a hexagonal intermetallic tube. These intermetallics form very rapidly, and are present in 60Sn-40Pb solder that is molten on Cu for only a few seconds.

intermetallic tubes present. Currently under investigation is a method to slow down the formation of the hexagonal intermetallic tubes.

Fatigue of Solder Joints

Equipment and specimens have been designed and built to test solder joints in fatigue and thermal fatigue. In order to test solder joints in shear the specimen configuration shown in Figure 10 was designed. This specimen closely imitates the

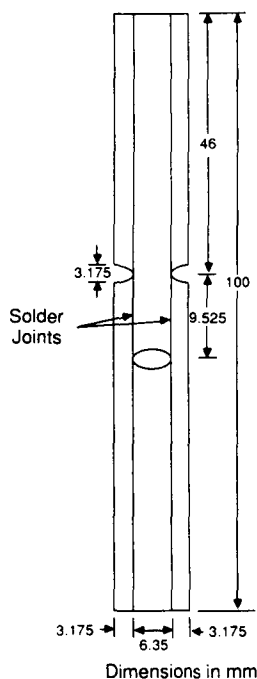


Figure 10. Specimen design to test solder joints in shear deformation for fatigue studies. The specimen consists of three Cu plates joined by two solder joints. The solder joints between the holes are deformed in shear when the specimen is gripped on opposite ends. In electronic packages the deformation of solder joints is most commonly found to be in shear.

loading conditions found in the solder joints of electronic packages. To test these joints a digitally controlled loadframe was designed and built (Figure 11). The loadframe is controlled by a computer that digitally sets the deformation cycle and collects data simultaneously. This equipment gives us the unique ability to test solder joints in controlled conditions. Tests are currently in progress to investigate the effect of strain, strain rate, number of cycles, and temperature on the fatigue life of solder joints.

Thermal fatigue tests are also in progress using the equipment shown in Figure 12 that was designed and built to investigate the effect of strain and temperature on solder joints. Specimens consist of sandwiches of materials of different thermal expansion coefficients soldered together. By cycling these specimens between two thermal baths (-55°C to 125°C) the effect of strain and temperature on the microstructure of solder joints can be understood.



Figure 9. Scanning electron micrograph of the fracture surface of 60Sn-40Pb solder that contains intermetallics failed in tension. The hexagonal rod-like nature is evident as is the solder core inside the intermetallic. The fracture is initiated at the interface between the intermetallic and the solder. The presence of these intermetallics has little influence on the strength of the solder but greatly decreases the toughness and fatigue life of the solder joints.

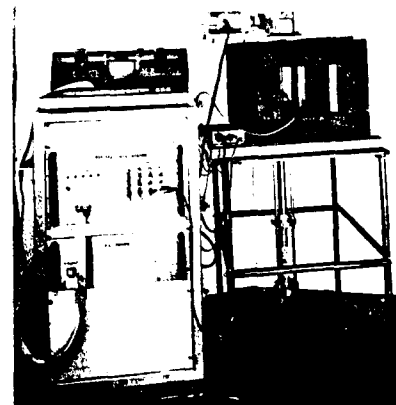


Figure 11. Digital loadframe designed and built to test solder joints in fatigue. The computer controls the loadframe so that accurate amounts of load and strain can be imposed on the specimen in fatigue. The computer also allows for the collection of data during testing.

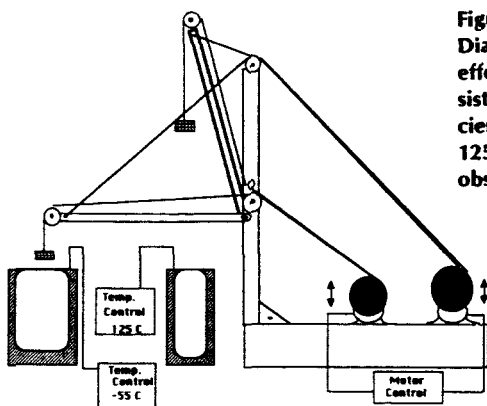


Figure 12.

Diagram of thermal cycling equipment designed and built to investigate the effect of strain and temperature on solder joints. The specimens tested consist of solder joints between metals of different thermal expansion coefficients. The equipment cycles specimens between thermal baths (-55°C to 125°C). Both microstructural changes and solder joint failures can be observed using this equipment.

Highlights of Other Research

The effect of ternary alloy additions to solder joints is also being studied. Additions of elements such as Ag, Bi, In, and Sb (which are common industrial alloy additions) are found to have an effect on both the microstructure and mechanical properties.

The stress relaxation properties of solder joints have also been studied. Initial results have shown high temperature relaxation to approximate bulk solder properties.

The future development of improved high-field superconducting magnets is critically materials-dependent. One application that requires improved materials in superconducting magnets is magnetic fusion energy reactors. The feasibility of such reactors is dependent on the ability to utilize superconducting magnets to minimize power consumption. Future designs for these magnets are limited by available superconductor materials and cryogenic structural alloys. Materials research is addressing needs for both the next-generation test reactor designs and improved metallurgical understanding of high-potential alloy systems.

The high current densities required at high magnetic fields (12–20 T) necessitate the use of advanced superconductors. The upper critical fields of A15 compounds such as Nb_3Sn and Nb_3Al greatly exceed those of the more conventional superconductors such as NbTi. Commercial production of Nb_3Sn is now achieved and this material is presently specified for use in new high-field magnet designs. Our results have provided a microstructural basis for improvements in the superconducting properties of these wires through heat-treatment and third-element modifications.

New materials are also required for the magnet cases of future high-field magnets. Designs for magnetic fusion reactors call for strength and toughness levels at 4 K beyond the capacity of existing materials. New high-Mn, high-N

MATERIALS FOR HIGH-FIELD SUPERCONDUCTING MAGNETS

austenitic steels currently under development show excellent potential for these applications. One concern is the ability to retain high strength and toughness levels in the welded condition. Control of weld metal strength levels has been achieved through additions of N to the shielding gas during welding. The dependence of 4 K toughness on chemistry modifications controlling the residual levels of delta-ferrite has also been demonstrated.

Superconductors

The superconducting properties of Nb_3Sn and Nb_3Al multifilamentary wires are strongly processing-dependent. Because the superconducting A15 phases are brittle intermetallics, the wires must be drawn prior to reaction using special processing methods. Two such methods used to produce Nb_3Sn are the bronze and internal-tin processes. To obtain a more fundamental understanding of the material and to guide further improvements, the microstructural determinants of the high critical currents measured in internal-tin wires were investigated. The two major sources of improved critical currents are increased Nb_3Sn in the cross-section and increased amounts of fine-grained Nb_3Sn . This microstructural basis was used to significantly shorten heat treatments used in an internal-tin wire produced by the Intermagnetics General Corporation.

The influence of third-element additions in bronze-processed wires fabricated at LBL was also investigated (Figure 13). Titanium and Mg additions were made to the Nb core and the Cu-Sn bronze, respectively. Microstructural evolution during heat treatment of these wires remained similar to a control wire. The beneficial influence of Ti additions is attributed to improvements in the quality of the A15 phase. The rapid Nb_3Sn layer growth with the high bronze/Nb ratio in our wires limits the effectiveness of Mg additions in refining the grain size while Mg adversely affects the drawability of the wires.

While Nb_3Al is a high-potential superconductor, critical current densities are presently limited by the volume fractions of the superconducting A15 phase that can be achieved. Substantial increases in the critical current densities require a fundamental understanding of the A15 reaction and its dependence on the unreacted microstructure. The thickness of the ribbon-like filaments of Nb and Al resulting from heavy reductions of powder wires (Figure 14a) is characterized by a drawing-index, defined as $(\text{Nb powder size})/(\text{Reduction ratio})^{1/2}$. The critical current density is found to scale well with this parameter for a wide range of wires. It is postulated that excessively thick Nb layers limit the reaction to A15. The evolution of phases during reaction of these wires were investigated by TEM. In regions where Nb and Al powders have agglomerated to form superlayers the extent of reaction is limited by the formation of the non-superconducting σ

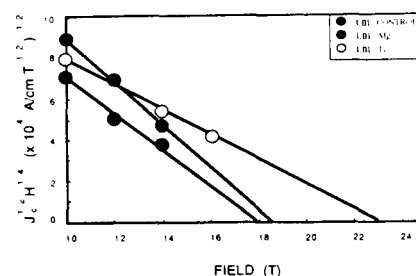


Figure 13. Kramer plot of the superconducting properties of LBL bronze-processed Nb_3Sn . The upper critical field increases from approximately 18 T to 23 T in a Ti-doped wire. Mg additions were not effective in refining the A15 grain size and decreased the drawability of the wire.

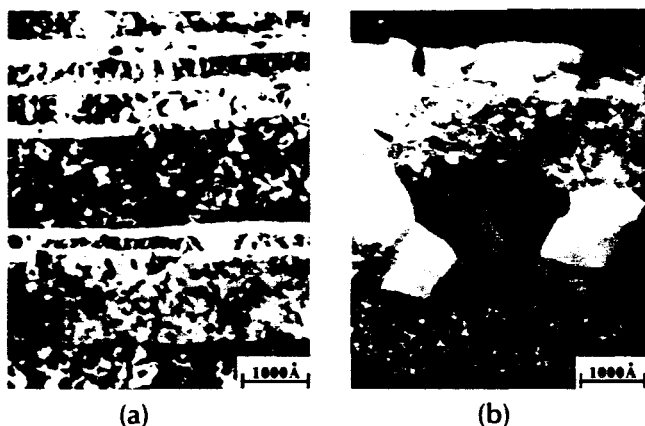


Figure 14. Longitudinal sections of Nb-5 wt.% Al powder wire: a) unreacted wire; dark, heavily dislocated layers are Nb. b) reacted 900°C/20 min + 750°C/2 days; a layer of sigma phase is sandwiched between two A15 layers. The clear equiaxed grains are the superconducting A15 phase (Nb₃Al). The remainder of the wire is unreacted Nb and non-superconducting sigma phase (Nb₂Al).

phase (Nb₃Al). The arrangement of layers in these areas is Nb/A15/ σ /A15/Nb (Figure 14b). To accurately determine the maximum layer thickness in the wires which allow complete reaction to A15, sputter-deposited layers with improved uniformity are being investigated.

Structural Materials

Needs for structural materials with improved cryogenic mechanical properties have stimulated the development of new high-Mn alloys. As a new class of alloys, improved fundamental understanding of their metallurgy is required. Of particular concern for current applications of these alloys is the ability to retain high cryogenic strength and toughness in the welded condition. Losses in the 4 K yield strengths of gas-tungsten-arc welds are found to be due to reductions in weld metal N content. The ability to manipulate the 4 K yield strengths through N additions to the shielding gas during welding has been demonstrated (Figure 15). The weld metal

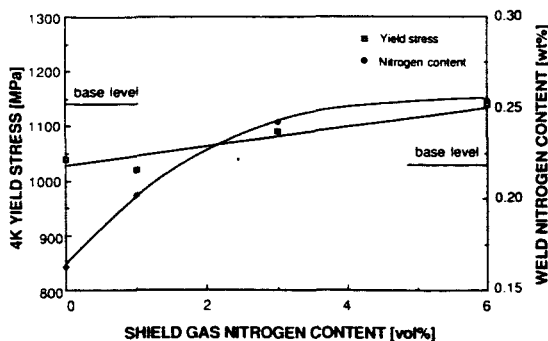


Figure 15. Weld metal nitrogen content and 4 K yield strengths can be controlled through nitrogen additions to the shielding gas in gas-tungsten-arc welds of a high-Mn steel (Fe-16Cr-5Ni-18Mn-0.22N).

toughness is also of concern. Microstructure-specific features on the fracture surfaces have been correlated with residual delta-ferrite phase formed during solidification. The increasing amounts of the ferromagnetic delta-ferrite phase in the weld that are measured by the magnetic permeability are related to losses in the 4 K toughness. Weld metal chemistry modifications to compensate for solute segregation during

solidification and to control the as-solidified microstructure are under investigation.

Both engineering usage and future developments in high-Mn alloys require improvements in our fundamental understanding of these materials. The sources of cryogenic intergranular embrittlement and the means necessary for its control in high-Mn steels are of particular concern. Previous results in binary Fe-Mn alloys show that while fully-austenitic alloys possess the best cryogenic mechanical properties, they suffer from susceptibility to intergranular fracture. The influence of chemistry modifications to binary Fe-31Mn alloys on the microstructures and the ductile-to-brittle transition behavior were examined. It is concluded that high-Mn alloys are inherently susceptible to intergranular embrittlement due to reduced grain boundary cohesion and planar deformation behavior conducive to the formation of high grain boundary stress concentrations. Grain boundary cohesion can be improved through limitation of the Mn content and the addition or redistribution of remedial solute species such as B and C. The cryogenic intergranular embrittlement is fully suppressed through appropriate chemistry modifications.

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Note:

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INSTRUMENTATION FOR SURFACE SCIENCE _____

INSTRUMENTATION FOR SURFACE SCIENCE

The Instrumentation for Surface Science Program is concerned with the development of new techniques and instruments for the study of surfaces. It has three experimental components:

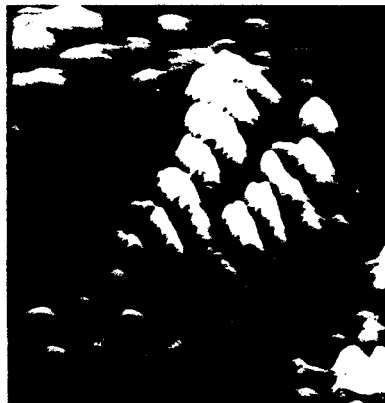
- Applications of the scanning tunneling microscope (STM)
- Investigations of surfaces by nonlinear optical techniques
- Studies of surfaces with infrared techniques.

In addition, the experimental work is supported by a theoretical component concerned with surfaces, interfaces and clusters.

The STM is a major new tool for surface science that is being used in many laboratories around the world. It is a unique tool for the study of both the topology and electronic properties of surfaces. Research at LBL, pursued in part with the funding from the IBM Corporation through a fellowship to E. Ganz, involves microscopes operating both in ultra-high vacuum and in air. Within the past year, atomic resolution of clusters of silver and gold on graphite atoms has been achieved, the unexpectedly large influence of surface contamination (for example, water) on the deformation and imaging of surfaces by the STM has been demonstrated, and the remarkable fact that one sees only every alternate carbon atom in the graphite surface has been explained by theorists Louie and Tomanek by means of a pseudopotential calculation, the predictions of which have been confirmed experimentally.

A new surface analytical tool using surface optical second harmonic generation has been developed to study organic monolayers on a liquid surface. In collaboration with workers from Exxon Research and Engineering Company, the technique has been used to measure orientations of molecules on water, to show that the two-dimensional liquid-expanded-liquid-compressed transition is characterized by a sudden change in the molecular orientation, to determine the nonlinearity of organic molecules, and to monitor the polymerization process of a monomer monolayer.

A new type of calorimeter has been developed to determine the heat capacity of thin layers of CO adsorbed on evaporated silver films. When the films are only a few monolayers in thickness, this heat capacity in the ^4He temperature range scales as T^2 , as expected for a 2-dimensional system. At greater thicknesses, the heat capacity scales as T^3 as expected for a 3-dimensional system.



The theoretical group is involved with a variety of calculations using *ab initio* pseudopotential techniques. There is a close collaboration with the experimental STM group to explain and predict relevant surface phenomena. The structural and high pressure properties of BN, BP and BAs, some of which may have asymmetries similar to those found in graphite, have been computed. A simple expression has been developed for computing the bulk modulus of a solid from its lattice constant.

SCANNING TUNNELING MICROSCOPE

The scanning tunneling microscope (STM) has the ability to resolve single atoms on the surface of electrically conducting samples. The heart of the device is a sharpened tungsten tip which is placed within a few angstroms of the surface under study. One determines the separation of the tip and sample with a precision of better than 0.1 Å by measuring the current that tunnels across the intervening gap. By moving the tip over the sample in a raster pattern by means of piezoelectric crystals, and maintaining either the tunneling current constant by moving the tip in or out, or the height of the tip constant by measuring the variations in current, one maps out the surface topography and/or electronic structure.

Over the past year we have investigated the surface of graphite with the STM operated both at atmospheric pressure and in ultra-high vacuum (UHV), and have explained the major effects of the presence of contamination by materials such as water on the sample surface. We have also studied metallic clusters containing a small number of atoms (typically fewer than 20) deposited on a graphite substrate.

We have obtained images of the surface of graphite primarily in the "current-imaging" mode, so that variations in tunneling current give information about the topology and electronic structure of the surface. With this technique we obtain a 24 Å × 24 Å image in one second. Figure 1 shows such an image on the surface of graphite. The grey (α) spots and white (β) spots correspond to adjacent carbon atoms in the honeycomb array. Surprisingly, they clearly exhibit an enormous asymmetry. The two types of atomic sites do differ, however, in that the α -sites have neighboring atoms in the atomic layer below while the β -sites do not (Figure 1). With the help of accurate *ab initio* calculations, this asymmetry has been traced to details in the electronic band structure of graphite near the Fermi energy E_F . The particular symmetries of the electronic states on the α and β atoms near E_F were shown by the calculations to cause an asymmetry in the corresponding charge densities in the narrow energy region sampled by the STM. Thus, the features observed experimentally are well explained by the theory. These results demonstrate the usefulness of the STM for investigating

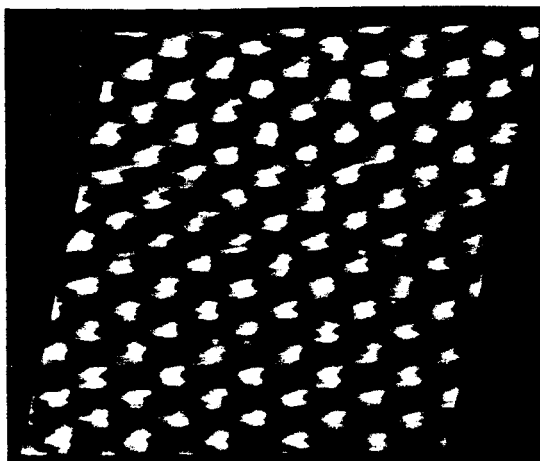


Figure 1.
STM image of a $24 \text{ \AA} \times 24 \text{ \AA}$ region of a cleaved graphite sample taken at constant tunneling tip height. The shading is fixed by the tunnel current: dark to light corresponds to 1.5 nA to 2.5 nA. The white spots and grey spots correspond to adjacent carbon atoms in the honeycomb ring, and are separated by 1.41 \AA . This large asymmetry between the two sites has been traced to details in the bulk electronic band structure near the Fermi energy E_F .

the fine details of electronic structure which, in this case, are strongly influenced by the atoms below the topmost layer. The danger of interpreting STM images simply in terms of atomic charge densities is also very well illustrated.

Images obtained in the constant-current (topographic) mode show additional anomalies, due to the presence of adsorbed contamination. First, we have observed unphysically large atomic corrugations of up to 24 \AA . Second, we find that one can continue to observe atomic structure when one moves the tip progressively in a direction perpendicular to the surface over distances as large as 100 \AA . Both observations can be explained by a model in which the tunneling tip physically deforms the graphite not by direct contact but by pushing on the surface through a layer of adsorbed contamination. The principal result of this model is that the change in gap spacing is only a fraction of the actual motion of the tip, because both the contamination layer and the graphite have non-zero compressibility. The large corrugations thus correspond to the absolute tunnel tip height, while the variations in actual tunneling gap are much smaller, being reduced in magnitude by the ratio of the compressibilities of graphite and contamination.

Similarly, deformation of the surface allows tunneling to occur over large excursions of the tunneling tip without a concurrently large change in gap resistance, since the contamination allows the tip to apply pressure over a large area of graphite while remaining electrically insulating.

We have tested for the effects of contamination by systematically cleaning the graphite surface. After we had placed the graphite in a UHV chamber operating in the 10^{-10} torr range and heated the graphite to 500°C for 1 hour, we observed the distance over which the surface was deformed to shrink from tens of angstroms to 1 \AA . At the same time, the corrugation amplitude shrank from the 24 \AA described above at atmospheric pressure to less than 1 \AA under clean conditions. Both results are a graphic demonstration of the effects of surface contamination.

We have also used graphite as a support for the study of small metallic clusters deposited by evaporation in an argon atmosphere. In the topographic mode, we were able to image the large Ag cluster shown in Figure 2. The cluster, which was evaporated on to the surface in an atmosphere of argon, is roughly 350 Å in diameter and 30 Å high. Close inspection of the figure reveals that the cluster is composed of several smaller agglomerations each 30 to 100 Å in diameter. The presence and shape of the smaller features suggests that the large cluster was formed by the coalescence of several smaller mobile clusters.

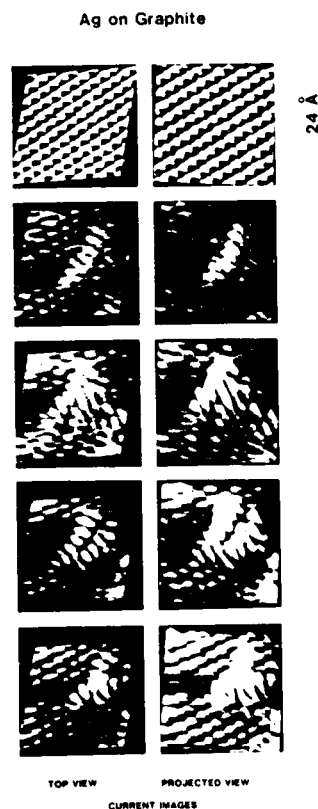


Figure 2. Top view of a large silver cluster on graphite taken in constant-current (topographic) mode. The image is 500 Å × 600 Å, and the grey scale corresponds to a total height variation of 40 Å from dark to light. The cluster is composed of several smaller agglomerations each 30 Å to 100 Å in diameter, suggesting that it was formed by coalescence of small, mobile clusters after deposition onto the graphite substrate.

Smaller regions are imaged with high resolution when the STM is operated in the current-imaging mode. As an example, in Figure 3 we show a series of five 24 Å × 24 Å images. The pictures on the left represent top views of the tunneling as a function of position, while the pictures on the right represent projected views of the same sets of data. Figures 3(b) and (b') show a Ag cluster roughly 15 Å long and 5 Å wide. The cluster appears to be made up of approximately seven groups of atoms. The feature at each end of the cluster could well be a single atom. Although the length of the inner five groups varies, the typical length of 4 Å to 5 Å is not inconsistent with the value expected for a Ag dimer, that is, two covalently-bonded Ag atoms. The bond length of a free Ag dimer has been calculated to be 2.1 Å to 2.4 Å. Because the electron charge density between the two atoms is high, it is plausible that the STM would not resolve the individual atoms. If we assume that the dimers are weakly coupled in the cluster via van der Waals forces, we

Figure 3.

Top view (a) and projected view (a') of 24 Å × 24 Å clean graphite lattice obtained in current-imaging mode, as shown in Figure 1; (b,b') through (e,e') illustrate the time evolution of a small silver cluster on the graphite substrate. Images (c,c') (d,d') and (e,e') were taken 15-1/2 min, 18 min and 23 min, respectively, after (b,b'). The cluster is apparently formed of a group of silver dimers which diffuse on the graphite surface.



would expect the individual dimers to be resolved. The STM has clearly demonstrated its potential as a tool for a wide variety of industrial applications. At present the IBM Corporation is supporting the program at CAM through a full fellowship to one of the students working on the project.

SECOND HARMONIC GENERATION

We have developed a new surface analytical technique to study monolayers of molecules adsorbed at an interface. The technique is based on a simple nonlinear optical effect — optical second harmonic generation (SHG) by a laser beam reflected from a surface. As a second-order process, SHG is forbidden in a medium with inversion symmetry, but is necessarily allowed at a surface or interface. Consequently, the process is highly surface-specific, and can be used to probe surfaces. The experimental setup for a typical surface SHG study is fairly simple, as shown schematically in Figure 4. As a laser technique, it has many advantages over conventional methods. It is sensitive, nondestructive, and capable of in-situ remote sensing. In addition, surface probing with high spatial, time, and spectral resolution becomes possible.

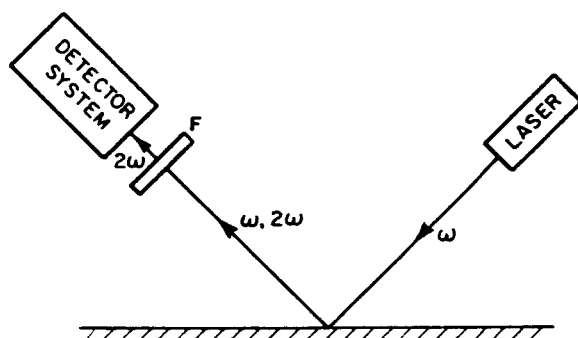


Figure 4. Surface studies by optical second harmonic generation require a rather simple experimental setup. As shown here, the second harmonic radiation is generated at the sample surface in the reflected direction by the incoming laser beam. It is detected by a photomultiplier after a filter system (F) which is used to block the reflected laser light.

We have applied the SHG technique to a number of problems concerning monolayers of molecules floating on a water surface (Langmuir films). First, in collaboration with Dr. M.W. Kim's group at Exxon Research Engineering Company, we used SHG to measure the orientation of molecules as a function of surface molecular density on water. The experimental arrangement is shown in Figure 5 and the results were correlated with the π -A (surface tension — surface area) diagram for the monolayer system. Two different surfactants of practical interest $\text{CH}_3(\text{CH}_2)_{11} - \text{C}_{10}\text{H}_6 - \text{SO}_3\text{Na}$ and $\text{CH}_3(\text{CH}_2)_{13} - \text{COOH}$ were studied. It was found, as expected, that in both cases the molecules tend to "stand up" more with increasing surface density. In the dense-packed limit, the average molecular orientations take the forms depicted in Figure 6. In the case of the fatty acid, we were able to show conclusively for the first time that the so-

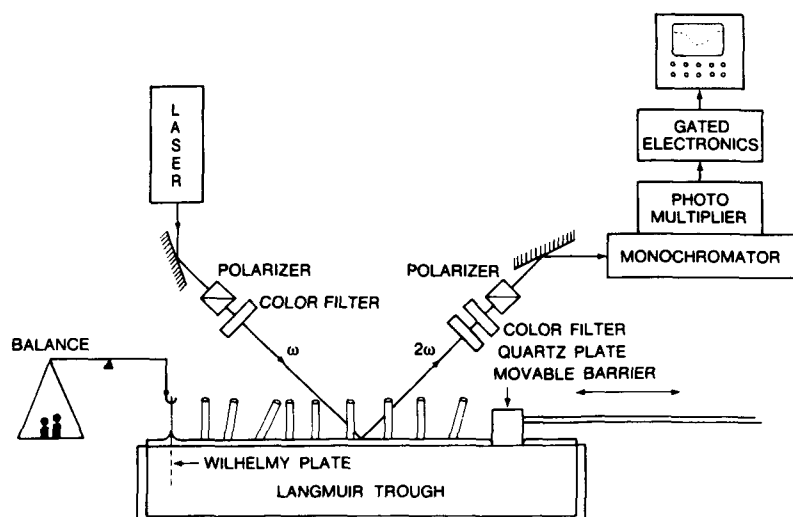


Figure 5.

The schematic diagram here shows the detailed experimental setup for simultaneous measurements of surface tension (π) versus surface area (A) and optical second harmonic generation from a monolayer of molecules floating on a water surface. The movable barrier varies the surface area per molecule and the balance measures the surface tension.

called liquid-expanded (LE) to liquid compressed (LC) transition for a Langmuir film is characterized by a phase transition in the molecular orientation.

Also in collaboration with the Exxon group, we demonstrated by measurements on a series of molecules that surface SHG from a Langmuir monolayer can be used to determine the optical nonlinearity of a molecule. This method is superior to the other methods because of its overall simplicity in both measurements and analysis. This is important in view of the current interest in finding useful organic nonlinear optical materials.

We have also succeeded in using surface SHG to probe the polymerization of a monolayer of monomers on water. The results suggest that it should be possible to use SHG to study the dynamics of this reaction which is an important problem in many applications of polymer films such as coating, adhesion, and lubrication.

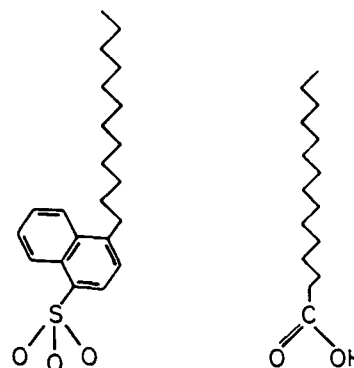


Figure 6.

Average orientation of molecules at an interface can be determined from the observed polarization dependence of the optical second harmonic generation. We show here the orientations of $\text{CH}_3(\text{CH}_2)_{11} - \text{C}_{10}\text{H}_6 - \text{SO}_3\text{Na}$ and $\text{CH}_3(\text{CH}_2)_{13} - \text{COOH}$ in a dense-packed monolayer on water.

A CALORIMETER FOR STUDIES OF THIN LAYERS ON METAL FILMS

We have built and characterized a novel calorimeter to measure the heat capacities of thin layers of material deposited on evaporated metal films. Existing calorimeters used to study adsorbed layers have consisted of some volume of highly porous material containing large areas of imprecisely defined surfaces. Such systems feature high sensitivity, but one often finds difficulty in completely cleaning and characterizing the surfaces at which the adsorption takes

place. In contrast, the calorimeter used in this study, shown in Figure 7, features an open, flat surface which, in these studies, is prepared by the evaporation of a smooth metallic film in an ultra high vacuum. Proper selection of materials and careful design have enabled the sensitivity of this calorimeter to exceed that of more conventional calorimeters, while providing a more easily prepared and characterized surface.

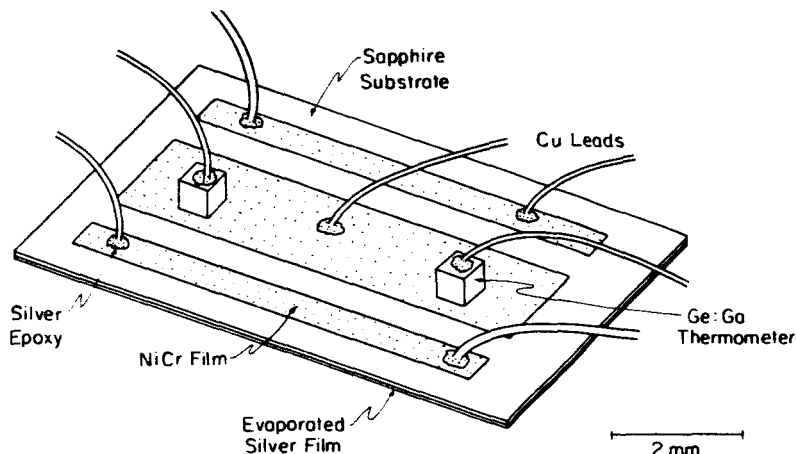


Figure 7. Schematic diagram of calorimeter for study of heat capacity of adsorbed layers deposited on the underside of the sapphire substrate.

We have used this calorimeter to study the heat capacity of thin layers of CO adsorbed on an evaporated Ag film in the temperature range of 2.7 to 4.3 Kelvin. For a single layer, it is expected from simple Debye theory that the heat capacity should be proportional to T^2 . However, as the films become thick enough to accommodate the long wavelength phonons typical of this temperature range, the temperature dependence of the heat capacity is expected to increase to T^3 . In Figure 8, we have plotted the exponent which results from a least-squares semilogarithmic fit to our experimental heat capacity data as a function of the exposure of the He temperature surface to a dosing beam of CO. The exposure is expected to be proportional to coverage. The figure shows that the deviation from T^2 takes place between 20 and 40 layers, and is fully T^3 at coverages of 60 layers.

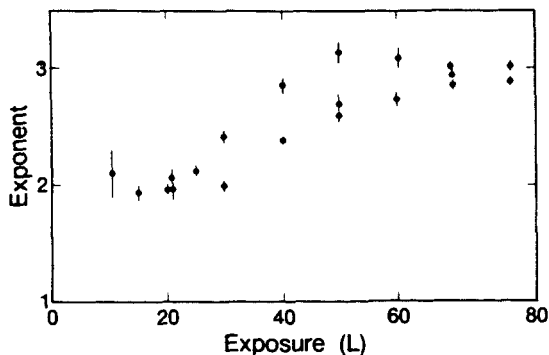


Figure 8. Exponent of the temperature dependence of the heat capacity vs. exposure for CO layers adsorbed on smooth evaporated Ag films. Each unit of exposure corresponds to one layer of CO molecules (1 Langmuir). The exponent changes from 2 for 2-dimensional films to 3 for 3-dimensional films.

This technique may readily be applied to many other combinations of adsorbate and overlayer, as well as studies of structural phase transitions in a single layer, superconducting transitions in thin metallic films, and wetting of adsorbed systems.

STAFF

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- Abraham, D.W., *STM: An Atomic Resolution Surface Science Technique*, Florida State University Seminar, Tallahassee, Florida, January 1986.
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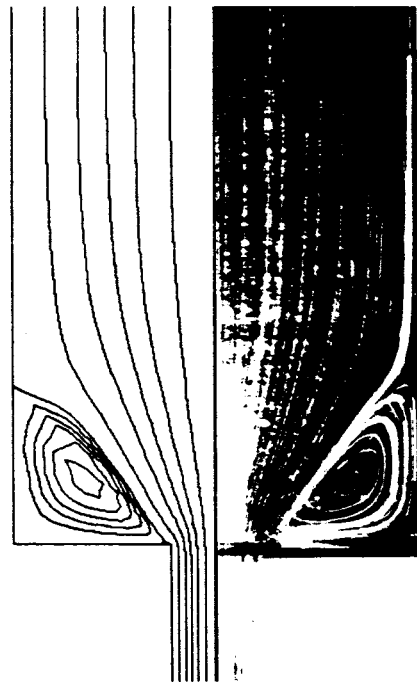
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Note:

Invited or Contributed Papers which subsequently appeared as Publications (refereed) or Other Publications (non-refereed) are listed in both applicable categories.



POLYMERS AND COMPOSITES

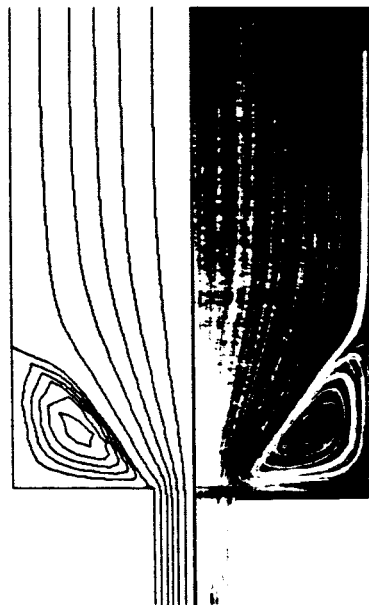
POLYMERS AND COMPOSITES

High performance polymeric materials are now being used in large-scale and load-bearing applications which in the past have demanded the use of metals. Understanding the development of high strength and rigidity in polymeric materials requires some molecular concepts which are not found in other branches of materials science. The long, essentially linear molecules of thermoplastic polymers can be extended or coiled. The degree to which the chains are extended, and the degree to which they are oriented in a single direction, extended or not, control the physical properties of the polymer. The technology of fabricating high performance polymeric systems involves ingenious routes to manipulating the distribution of molecular and supramolecular orientations. This microstructure is determined to a large extent by how processing and shaping are carried out in the liquid state; liquid state shaping usually involves subtle interactions between cooling rates and deformation history and the control of phase changes.

The CAM Polymers and Composites Program has focused on the generic problem of the prediction and control of structure development since its inauguration and planning Industrial Workshop in October, 1983. The primary emphasis has been on two closely interrelated problems:

- the development of computational tools for the prediction of structure development in complex shaping flows, and
- the analysis of structure development in anisotropic (usually heterogeneous) materials. These anisotropic materials, which include liquid crystal polymers and multiphasic polymeric systems, encompass the major areas of opportunity for significant advances in high-performance polymers.

Our computational research has led to the development of an accurate and efficient approach to the prediction of shapes, stress distributions, and instabilities when there is a polymer/gas interface. CAM researchers, guided by calculations on the CRAY X-MP supercomputer and extrusion experiments, have identified a physical basis for the general failure of researchers worldwide to be able to predict polymer flow and structure development in complex mold shapes; this work has demonstrated the need for a better understanding of the interactions between a polymer melt and a metal surface. CAM numerical computation and coordinated experiments have established the methodology for the prediction of orientation (and hence structure) in lightly-filled short-fiber polymer composites.



Much of the work on anisotropic materials has focused on liquid crystal polymers, which were characterized by Workshop participants as "one of the most exciting advances in the last 15 to 20 years in polymer science...". These materials are characterized by micron-scale "domains" in the melt, and the domain flow and orientation determines macroscopic properties. CAM researchers have recently used solid state Nuclear Magnetic Resonance spectroscopy (NMR) to establish the existence of crystalline phases with compositions radically different from those of the bulk material in certain of these polymers. Other experiments have established the existence of a configuration-dependent creep of the liquid crystalline materials in submicron regions "between" domains; this behavior appears to be a major factor in determining orientation in the core of a mold. Work on "molecular composites", in which the rod-like polymer is blended with an isotropic matrix, has led to a formulation enabling prediction of the stress state and orientation distribution in the composite.

Other heterogeneous materials that are being studied include block copolymers, which are phase-separated systems in which manipulation of interphase dimensions and compositions could lead to superior properties and property control. CAM researchers have succeeded in using Transmission Electron Microscopy (TEM) to determine composition profiles in the approximately 30 Å interphase with a resolution of 3 Å. CAM work on the analysis of anisotropic membranes, which is now coming to an end, resulted in the ability to predict phase separation kinetics; the theory that was developed motivated the development of a thermal process for the manufacture of asymmetric membranes, for which patent applications have been filed.

CAM polymer research has already received a substantial amount of recognition. The work on computational methods, on flow instabilities, and on structure development in liquid crystals have all been subjects of invited talks at major international meetings. Program Leader Morton Denn was elected to the National Academy of Engineering and received the Bingham Medal from the Society of Rheology in 1986. Denn and Division Fellow Roland Keunings are two of the co-chairmen of the next biennial International Workshop on Numerical Methods in Non-Newtonian Flow.

The Industrial Advisory Board for the Polymers and Composites Program meets annually. The Board includes representatives from DuPont, Celanese, IBM, Dow U.S.A., and Exxon Research and Engineering. Financial support has been received from DuPont and the Dow Chemical Company Foundation. A donation of equipment was made by Rheometrics, Incorporated. Non-commercial polymers for research have been supplied by Celanese, Eastman Chemicals, and DuPont.

The nonquantifiable interactions with industrial scientists have had a significant impact on the development of the research program. There have been many hours of fruitful discussions regarding experimental design and technique with industrial scientists from a number of corporations, particularly Raychem, Celanese, DuPont, Chevron, Dow, Owens-Corning Fiberglas, and Union Carbide, both at corporate research laboratories and at CAM. One joint research publication has resulted with scientists from Dow. Researchers at a number of these corporations have also made measurements for us, to do characterization not possible here or to provide a check on experimental methods. CAM researcher David Soane spent a portion of his sabbatical leave at the IBM Research Laboratories in San Jose.

COMPUTATION AND MODELING

The focus of this research is on the use of advanced computational techniques in order to predict structure development during shaping in the liquid state. The work can be broadly characterized into three subareas, as follows:

- transient finite element techniques for free-surface deformations of viscoelastic liquids,
- finite-element analysis of confined shaping flows, and
- thin sheet/thin filament analyses of viscoelastic flows with free surfaces.

The focus on free-surface flows is motivated by the fact that liquid/gas free-surface interfaces exist in many complex shaping operations, and the flow and flow-induced orientation in the neighborhood of the free surface is a critical factor in determining bulk morphology.

We have developed efficient finite-element algorithms for transient, free-surface deformations of polymeric liquids, some of which have been implemented on the National Magnetic Energy Fusion Computer Center (NMEFCC) CRAY X-MP at Livermore. This has enabled us to study the dynamics of surface irregularities and the deformation of low-viscosity inclusions in heterogeneous media. This methodology, which is still being improved upon, provides a powerful tool for the analysis of stress and structure development in an important class of polymer flows.

We have at the same time developed thin filament/thin sheet methodology for the analysis of certain free-surface flows, and we have established some guidelines in which this methodology is adequate to replace the more expensive finite-element approach. We have utilized this approach to discover regions of high sensitivity and complete flow breakdown in free-surface processing.

The major outstanding problem in the analysis of orientation development in confined shaping flows centers on

what is known as the "high Weissenberg number problem", which is a failure of all computational algorithms to converge to a solution for realistic values of material properties. This problem has been the focus of the series of biennial international workshops. Our CAM research, motivated in large measure by calculations done on the CRAY X-MP supercomputer, and supplemented by singularity analysis and extrusion experiments, has established that the general description of polymer stress development in the neighborhood of mold corners and lips is likely to be incorrect, and that some of the numerical problems are in fact a consequence of incorrect modeling of the polymer melt/metal surface interaction. A major research effort is needed in the area of polymer melt/metal surface interaction. The singularity does not arise in analyzing the flow of fiber suspensions for use in composites, and we have demonstrated, through comparison with CAM experiments, that finite-element calculations utilizing a new continuum theory for lightly-loaded fiber-filled composites provides an accurate description of the fiber orientation.

Finite-Element Analysis of Free-Surface Flows

Free-surface flows occur commonly in the processing of polymeric liquids. The orientation and structure in the shaped object is greatly influenced by the motion of the free (liquid/gas) surface, and there is no way of controlling this surface deformation locally. It is thus important to gain a comprehensive understanding of the mechanics of such free surface deformations.

We have developed a new computational scheme that enables us to follow the evolution of shape and structure during transient free-surface flows. This novel technique has been implemented on the NMEFCC CRAY X-MP supercomputer, and it has been demonstrated on several test problems. Improvements are continuing, with the goal of effecting savings in computing time and cost.

The growth of a disturbance on a polymer jet is a particularly good test problem, because experimental data exist and the deformation mechanics are known to differ significantly for macromolecular and low-molecular weight materials. Figure 1 shows the comparison of the growth of a surface disturbance on polymeric and low molecular weight filaments; the polymeric filament distorts more rapidly, but appears to stabilize, while the disturbance on the low molecular weight filament continues to increase until breakage occurs. This difference in behavior is consistent with experimental observations that have been reported in the literature for nearly 20 years, but have never been explained quantitatively. This new computational technique, together with a complementary "thin filament" analysis described subsequently, provides quantitative prediction of the

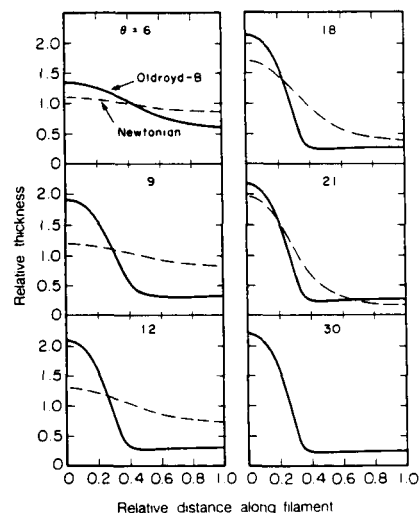


Figure 1. Computation of the dynamics of the growth of a surface disturbance on a polymeric filament (labeled "Oldroyd-B") and a low molecular weight liquid filament ("Newtonian"). θ is dimensionless time. The polymer initially deforms more easily, but it develops an apparent "strain hardening" and stabilizes, while the low molecular weight liquid continues to deform and breaks up.

disturbance growth on polymeric filaments for the first time, as shown in Figure 2. There are three regimes that are important in a deformation of the free surface: an initial relaxation period following shear flow during extrusion, an exponential growth regime, and a retarded growth resulting from the resistance of macromolecules to extensional deformation. The first and third regimes are unique to polymeric materials.

Confined Complex Flows

The prediction of flow patterns and stress and structure development in the complex geometries used for shaping flows requires advanced numerical techniques. The relationship between stress and deformation history (the *rheology*) of polymeric liquids is viscoelastic, meaning that the entire history of the the deformation governs the stress state; continuum descriptions of such liquids are in terms of partial differential or integral equations. All attempts to develop computational algorithms for polymeric liquids in complex shapes (containing corners or lips, for example) fail when a dimensionless parameter characteristic of the fluid memory reaches a critical value; this is known as the "high Weissenberg number problem," and has been the primary focus of several international workshops on numerical methods in non-Newtonian fluid mechanics. This problem must be solved before stress and orientation calculations that are meaningful under normal industrial conditions can be done with confidence. Our calculations on the NMEFCC CRAY X-MP supercomputer have demonstrated that the convergence problem occurs at increasingly lower values of the Weissenberg number with increasing resolution of the finite-element grid, and suggests that convergence could never be obtained with perfect resolution. The resolution used in these calculations is shown in Figure 3. The implication of this calculation is that the problem has a physical basis, and is not associated with numerics per se.

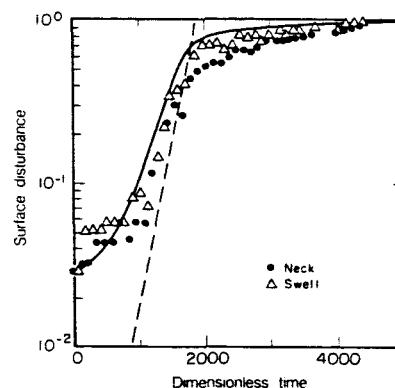
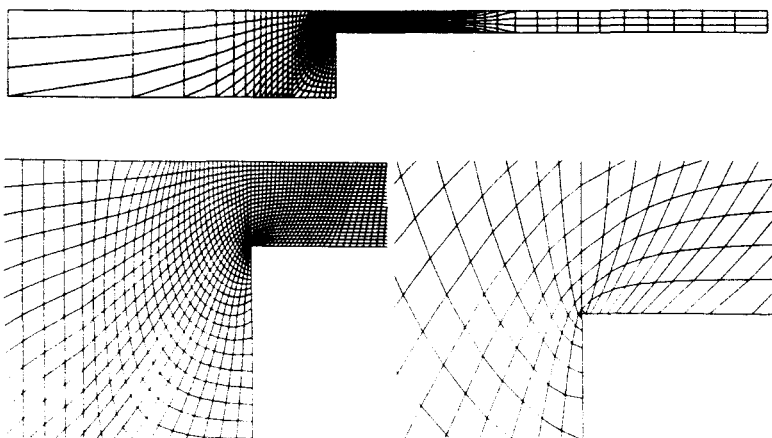


Figure 2. The predicted growth of the surface disturbance on a polymeric filament, together with experimental data originally published by Chin. There are three distinct regimes of growth; the first and third are unique to polymeric materials, and the third is predicted here for the first time.

Figure 3. The finite element grid used for the calculation of flow and stress development in a complex shape. The degree of spatial resolution utilized here is possible only with the use of the CRAY X-MP supercomputer.

We have subsequently shown that the full problem for polymeric liquids is singular in a strict mathematical sense, and that the singularity can apparently be overcome only by a reformulation of the physical description of the interaction between the polymeric liquid and a metal surface in regions where stress concentrations are likely to occur. This latter observation is supported by experiments which we have carried out on the extrusion of linear low density polyethylene, which indicated a failure of adhesion between the liquid polymer and the metal surface beyond some critical stress, as well as by claims in some recently issued industrial patents. A typical extrudate obtained during periods of particle wall slippages is shown in Figure 4. Our work demonstrates the necessity of a major research effort in the



Figure 4.
Surface of an extrudate of linear low density polyethylene obtained during a period of partial wall slippage.

area of polymer melt/metal surface interactions, which appear to be far more complex than those for low molecular weight liquids.

When the liquid is filled with high aspect ratio fibers, as in many structural composite materials, the macroscopic properties are determined by the properties of both the matrix and the fibers, and particularly by the orientation distribution of the fibers. Prediction of properties is thus critically dependent on the ability to predict the fiber orientation. We have developed a continuum theory for a special case in which fibers interact with one another only occasionally, and the matrix is not viscoelastic; this case is restrictive, but it is appropriate to some matrix materials and represents a first step towards understanding the behavior of the highly-loaded systems of practical interest. Our experiments have shown that the presence of even small amounts of fiber can cause large qualitative changes in the shaping flow, and hence in the fiber orientation. Finite-element calculations using the continuum theory predict these effects quantitatively; Figure 5 shows both experimental and computed flow patterns. The fiber orientation in these pictures is tangential to the illustrated flow lines.

Thin Filament/Thin Sheet Approximations

Many shaping and forming operations involving free surfaces utilize geometries which can be approximated by using special theories appropriate to thin filaments and thin sheets, thus reducing the mathematical complexity of the

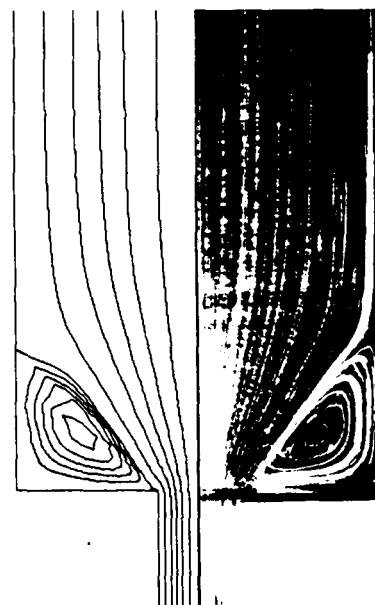


Figure 5.
Experimental and computed flow lines for a dilute suspension of chopped glass fibers. The fiber orientation is tangential to the flow lines. The size of the large recirculating region is four times that which would occur in the absence of the fibers. This is the first such prediction of this gross change in fiber orientation; all previous computational methodology has assumed that the fiber orientation would follow flow lines appropriate to an unfilled system.

predictive equations. The theoretical curve in Figure 2 was in fact computed using a thin filament theory, which was shown to be equivalent to the transient finite-element calculation for the particular case studied there. We selected the blown film process for biaxially oriented sheets as a system for detailed study, because it is an important shaping process in its own right and it contains features which appear commonly in polymer shaping operations: free surfaces, multi-dimensional stress fields, complex rheology, and large changes in physical properties because of temperature changes. The thin filament description was known to be applicable to this system because of prior work, including our own collaboration with Dow scientists on the simulation of the mechanics of drawn hollow tubes. Some typical results of the thin filament analysis for modeling the process behavior are shown in Figure 6. There are multiple intersections for lines of constant

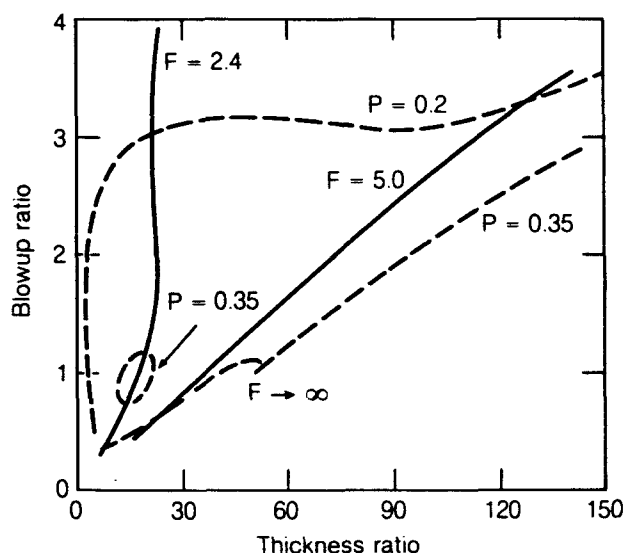


Figure 6. Operating diagram for biaxially-oriented film using the blown film process. The contours are lines of constant operating parameters: internal pressure and draw tension. Intersections indicate possible operating states; multiple intersections indicate that more than one film shape and orientation profile can occur for given operating conditions. The shapes of the contours, which depend on polymer properties, demonstrate that sudden transitions will occur following small changes in process parameters.

operating parameters, leading to multiple possible shapes and orientation distributions under identical processing conditions. Regions of the operating plane are inherently unstable. Because of the shapes of the contours, there will be situations in which small changes in operating parameters will result in conditions where steady operating is impossible. This study establishes the inherent sensitivity of the free surface process to very small changes in processing parameters. Polymer rheology plays an important role in the shapes of the opening parameter contours, and process operability and stability can therefore be greatly enhanced by changes in polymer structure that will lead to necessary changes in the rheology.

ANISOTROPIC AND HETEROGENEOUS MATERIALS

The focus of this research area is on the development and control of microstructure in heterogeneous materials.

Two broad classes of materials types have been studied, as follows:

- anisotropic materials, including liquid crystal polymers and short-fiber polymer composites, and
- phase-separated systems, including block copolymers and anisotropic polymer membranes.

There are close connections between the two broad categories and the subareas within each category.

The properties of liquid crystal polymers are determined by the size and orientation of "domains" and the apparent presence of residual crystalline phases during melt processing. We have identified crystalline phases by using solid state NMR spectroscopy. We have demonstrated a configuration-dependent creep of liquid crystalline materials in sub-micron regions between "domains"; this creep appears to be a major factor in determining orientation in the core of a mold, and we are currently working to develop the theoretical foundations to enable exploitation of this phenomenon.

We have demonstrated theoretically and experimentally how the presence of small amounts of short fibers changes the flow distribution in a mold, and hence determines fiber orientation. The extension of these results to the highly-filled systems of industrial interest is intimately related to the theory for liquid crystal polymers. Work on "molecular composites", in which a rod-like polymer is blended with an isotropic matrix, has led to a formulation enabling prediction of the stress state and orientation distribution in the composite.

The development of morphology in phase-separated systems is a kinetic process. We have developed predictive ability for phase separation kinetics in anisotropic membranes, and the theory that was developed led to a thermal process for the manufacture of asymmetric membranes (for which patent applications have been filed). We have utilized TEM to determine composition profiles with a resolution of 3 Å in the interphase of block copolymers.

Liquid Crystal Polymers

Liquid crystal polymers contain rigid segments in the backbone which cause them to exist in a highly-oriented ("mesophase") state in the melt. This orientation is localized into micron-sized "domains"; the domain structure can be seen in Figure 7, which is an optical micrograph obtained using polarized light. (The polymer shown in Figure 7 is a thermotropic polyester recently synthesized by CAM researchers.)

Melt-processible liquid crystal polymers, which are typically copolyesters, are semicrystalline. We have used solid state NMR spectroscopy to study crystal structure and composition. The existence of small amounts of crystalline phases in a copolymer of p-hydroxybenzoic



Figure 7.
Optical micrograph of the copolymer $[-\text{CO}-\phi-\text{CO}-\text{O}-\phi-\text{O}-\text{CO}-\phi-\text{O}-(\text{C}_2\text{H}_4\text{O})_2-]$ using polarized light, magnification 1500 \times . Dark and light regions are a result of local orientation in "domains" with a length scale of about 1 μm .

acid/poly(ethylene terephthalate) was established using proton spinlocking. Rigid domains were characterized with ^{13}C NMR using techniques that isolate the rigid phase; NMR traces are shown in Figure 8 for a copolyester containing 60% p-hydroxybenzoic acid.

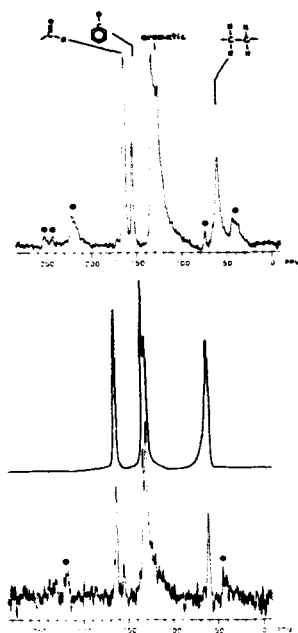


Figure 8.
Solid-state NMR trace of a copolyester containing 60% p-hydroxybenzoic acid and 40% poly(ethylene terephthalate). The upper trace is a ^{13}C NMR trace of the entire polymer, while the lower trace utilizes a technique that enables studying only the rigid component. The insert is a trace of poly(ethylene terephthalate) crystals, showing that the rigid phase is almost pure poly(ethylene terephthalate).

The crystalline phase is shown to consist entirely of poly(ethylene terephthalate). In the copolymer containing 80% p-hydroxybenzoic acid, in contrast, the crystalline phase is shown to be pure p-hydroxybenzoic acid. The composition of the crystalline phase is affected by the cooling rate in the 60% copolymer, and distinct crystal phases of p-hydroxybenzoic acid and poly(ethylene terephthalate) can be formed.

The kinetics of orientation and relaxation of domains in the melt were studied using variable-strength magnetic fields, with wide-angle X-ray diffraction to determine macroscopic orientation. Typical orientations are shown in Figure 9 for

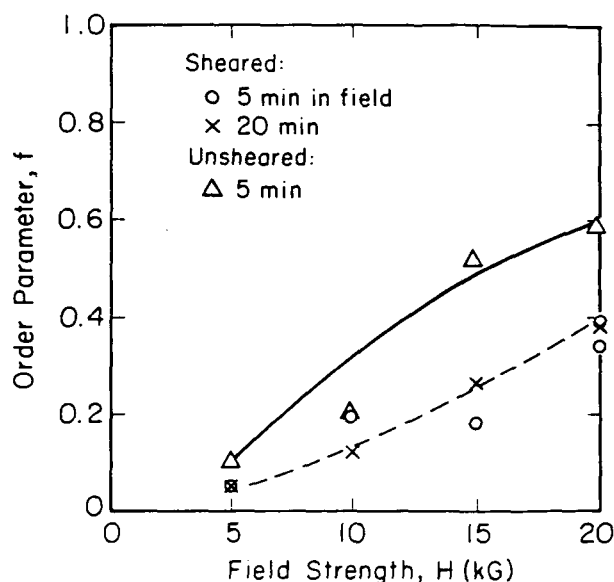


Figure 9. Orientation induced in a liquid crystal copolyester of 50% hydroxy naphthoic acid, 25% terephthalic acid, and 25% hydroquinone using a magnetic field. Greater orientation is obtained for samples which have not been presheared, indicating that shearing reduces the size of the domains.

sheared and unsheared samples. This work establishes that orientation kinetics are controlled by the deformation of the material in the sub-micron regions between the optically-observable domains. The deformation of such material is elastic and recoverable in classical liquid crystal theories, whereas there is creep and incomplete recovery for the polymeric systems. This phenomenon will be critical in determining orientation in regions of relatively low deformation rate, such as the core of the mold. The manner in which the inter-domain regions deform is not understood, and a theoretical study has now been initiated.

Work on describing the orientation of fibers in molded composites, and hence enabling prediction of macroscopic properties of the composite, has already been described in the preceding section and illustrated in Figure 5. It is believed that the blending of small amounts of rigid molecules with an amorphous matrix could lead to "molecular composites" having properties comparable to continuous-fiber composites, but processible by conventional techniques for homogeneous systems. We have developed a theory which enables computation of the angular distribution function characterizing the orientation of the rigid molecule; the stress exhibited by the composite is determined by the orientation distribution and the state of the matrix deformation. The theoretical methodology is similar to that used in developing the continuum theory for short-fiber composites.

Phase-Separated Systems

The domains in block copolymers are of order 300 Å, while the "interphase" (mixed) regions are of order 30 Å.

Manipulation of interphase dimensions and composition promises to lead to superior properties and property control. We have succeeded in using TEM to view the domains and interphase without distortion or ambiguity of lateral dimensions; computer software developed at the University of California San Francisco and Lawrence Livermore National Laboratory was utilized to enable a complete three-dimensional reconstruction of the microstructure. A typical composition profile is shown in Figure 10 for a styrene-butadiene block copolymer; the length scale on the abscissa is of order 30 Å, and data points are spaced only 3 Å apart. The results show that the interphase is slightly polystyrene rich and is not symmetric. Work is continuing to determine structural changes imposed *in situ*, utilizing the Kratos 1.5 Mev Transmission Electron Microscope at the National Center for Electron Microscopy.

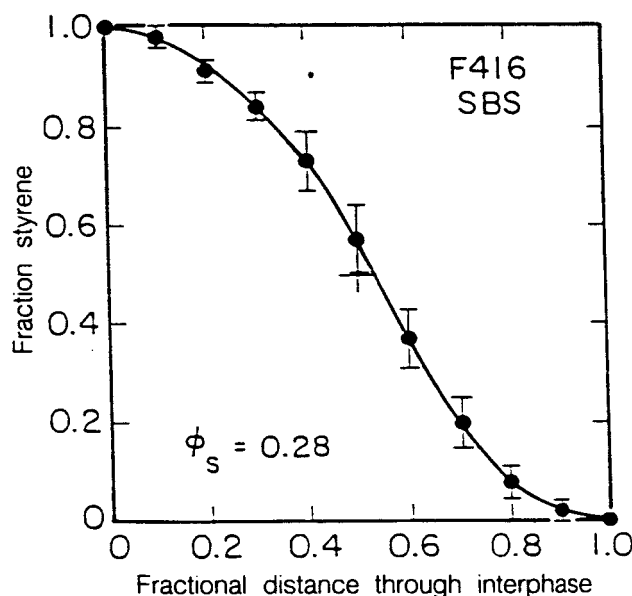


Figure 10. Composition profile in a styrene-butadiene block copolymer obtained using Transmission Electron Microscopy. The length scale on the horizontal axis is 30 Å, with an experimental resolution of 3 Å.

We have developed a theoretical analysis for the prediction of phase equilibria and phase separation kinetics in ternary systems. The initial work in this area suggested a new approach to the use of thermal gradients for the creation of asymmetric membranes, and subsequent successful experimental demonstration led to filing of a patent application. Recent work is focused on the use of systems containing short rod-like molecules; such ternary systems hold particular promise as optical storage media. Preliminary experiments using the system polystyrene-toluene-N-(4-ethoxybenzylidene-4'-n-butylaniline) (EBBA) are in good agreement with the equilibrium thermodynamic calculations.

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Lipscomb, G.G., R. Keunings, G. Marrucci, and M.M. Denn, *A Continuum Theory for Fiber Suspensions*, IXth International Congress on Rheology, Acapulco, Mexico, October 1984. (Proc. IXth International Congress on Rheology, vol. 2, p. 497, 1984.)

Note:

Invited or Contributed Papers which subsequently appeared as Publications (refereed) or Other Publications (non-refereed) are listed in both applicable categories.



INDUSTRY PARTICIPATION

INDUSTRY PARTICIPATION

One of the unique features of CAM as a research center in a national laboratory is the degree of emphasis on its interaction with U.S. industry. This effort is coordinated through an Industry Participation Office with the strong support of the leadership of each research program. During 1986 efforts focused on a number of areas.

- program advisory boards
- visits of industry scientists and research executives
- industrial fellowships
- research contracts and gifts
- equipment and materials donations
- proprietary information agreements
- technology transfer
- research collaborations



Program Advisory Boards

Each CAM Program is supported by a Program Advisory Board made up primarily of industrial research managers serving two or three year terms. The boards meet once each year to review the focus and goals of the program and the research progress made since the last meeting. A report is prepared on these aspects of the program with specific suggestions and criticisms. Advisory board members are shown in Table 1.

PROGRAM	NAME	COMPANY
Electronic Materials	R.A. Burmeister (Chairman)	Hewlett-Packard Company
	R.S. Bauer	Xerox Corporation
	W. Brown	AT&T Bell Laboratories
	J. Carruthers	Intel Corporation
	R. Reynolds	DARPA/Department of Defense
	R.N. Thomas	Westinghouse Electric Corporation
	A.F. Witt	Massachusetts Institute of Technology
Polymers and Composites	M. Panar (Chairman)	E. I. Du Pont de Nemours & Company
	J. Economy	IBM Research Laboratory
	J.D. Moseley	Dow Chemical Company
	D. Pearson	Exxon Research & Engineering Company
	J. Riggs	Celanese Research Company
Surface Science and Catalysis	J.A. Rabo (Chairman)	Union Carbide Corporation
	M. Boudart	Stanford University
	T. Clough	Atlantic Richfield Company
	M.L. Good	Allied-Signal Corporation
	J.P. Iesson	E. I. Du Pont de Nemours & Company
	P.J. Lucchesi	Exxon Research & Engineering Company
Structural Materials	P.E. Bretz (Chairman)	Aluminum Company of America (Alcoa)
	G.R. Chanani	Northrup Corporation
	R.C. Dorward	Kaiser Aluminum & Chemical Corporation
	S.L. Langenbeck	Lockheed Corporation
	A.L. Wingert	The Boeing Corporation
Ceramic and Metal Interfaces	R. Tummala (Chairman)	IBM, T.J. Watson Research Center
	G. Garrettson	Hewlett-Packard Company
	R.K. Shukla	Intel Corporation
	J. Stringer	Electric Power Research Institute
	I. Smith	General Motors Research Laboratories

TABLE 1

CAM ADVISORY BOARD MEMBERS

Industry Visits

Representatives from 46 industrial companies (Table 2) visited CAM during 1986 for periods of from one day to a week. Several organizations visited more than once; in most cases visiting a number of CAM programs. The focus of most initial visits was an exchange of information on current activities, with more detailed discussions of areas of mutual interest. It is expected that many of these contacts will lead to more detailed exchanges and collaborations.

One and two day detailed presentations of current and projected work in CAM were made to groups of research executives of two companies as a means of advising them of the novel areas of research and instrumentation at CAM.

Air Products and Chemicals, Incorporated	J. M. Huber Corporation
Alcoa Laboratories	J.T. Baker Chemical Company
Ambor Chemical	Kaiser Aluminum & Chemical Corporation
American Hoechst Corporation	Lester B. Knight and Associates, Incorporated
Amoco Research Center	Mallinckrodt, Incorporated
Ashland Chemical Company	Minnesota Mining & Manufacturing Corporation
Borg-Warner Corporation	Mitsubishi Research Institute
Brown Boveri, Incorporated	Mobil Research and Development Corporation
Catalytica Associates, Incorporated	Monsanto Company
Chevron Research Company	Morton Company
Clays & Aluminas	The P. Q. Corporation
Corning Glass Works	The Procter and Gamble Company
Dexter Corporation	Research & Development International
E.I. Du Pont de Nemours & Company	Rohm & Haas
Eastman Kodak Company	Shell Development Company
Engelhard Corporation	Sohio Chemical Company
Exxon Research & Engineering Company	Stauffer Chemicals
F.M.C. Corporation	Suedchemie
General Dynamics	Union Oil Company of California
General Motors	United Catalysts, Incorporated
Georgia Institute of Technology	W. H. Gauvin
Haldor Topsoe (USA & Denmark)	W. R. Grace & Company
Harshaw/Filtrol Partnership	Whirlpool Corporation

TABLE 2

COMPANIES SENDING VISITORS TO CAM

Industrial Fellowships

The Industrial Fellows Program at CAM is one of our most effective means of technology transfer to industry. Under the program, senior industrial scientists come to CAM to spend three months to a year as integral members of one of the research programs. Industrial Fellows not only pursue research projects while in residence, adding their own background and experience to that of the other programs staff, but also serve as excellent technology transfer agents when they return to their employer's laboratories. Their presence at LBL and CAM constitutes a substantial financial as well as technical contribution by their employers and can thus be regarded as a measure of the value of the CAM programs to industrial research efforts. Two Industrial Fellows worked at CAM during 1986 (Table 3), five are scheduled for

PROGRAM	FELLOW	COMPANY
Catalysis	Steven Potlock	Exxon Research & Engineering Company
Electronic Materials	Timothy Sands	Bell Communications Research

TABLE 3

CAM INDUSTRIAL FELLOWS

appointment in 1987 and more are expected in the coming years, once space becomes available in the new CAM buildings.

The value of this program has been recognized at the Department of Energy. Arrangements have been made for DOE support of the living expenses and travel of the Industrial Fellows while at work at CAM during this coming year through the Industry-Laboratory Technology Exchange Program.

Contracts, Gifts, and Fellowships

Unrestricted gifts during 1986 amounted to \$90,000 (Table 4). This type of funding is the most valuable to the

PROGRAM	COMPANY
CAM	Anonymous
Structural Materials	Aluminum Company of America (Alcoa) Xerox Corporation
Polymers and Composites	E.I. Du Pont de Nemours & Company Dow Chemical Company
Surface Science and Catalysis	E.I. Du Pont de Nemours & Company Chevron Research Company

TABLE 4

GIFTS TO CAM

programs because it allows them flexibility to deal with the most important and urgent research needs as they arise.

Three research contracts and one fellowship awarded in 1986 totaled \$103,000. The contracts serve to accelerate work on specific projects and enable the sponsors to maintain



Figure 1.
Philip E. Bretz, (left) Program Manager, Aluminum-Lithium Research and Development at Alcoa Laboratories, presents a check to LBL Director David Shirley. The \$50,000 unrestricted gift supports research in CAM's Structural Materials Program under the direction of Professor J.W. Morris (right).

close contact with the investigators and students and with results they obtain. The Surface Science and Catalysis Program has been working with companies in the catalyst manufacturing industry, the Structural Materials Program with the aerospace industry. A large number of CAM students are also supported on industrial and other types of fellowships administered through the University of California.

Proprietary Information Agreements

Proprietary information agreements were signed or continued between three companies and the Structural Materials and the Polymers and Composites Programs of CAM. These involve use and study by CAM investigators of highly proprietary samples of new materials provided by industry. Results of this work will be, by University of California and Lawrence Berkeley Laboratory policy, published in the open literature or in student theses, without compromising the confidentiality promised the donors.

Equipment and Materials Donations

Equipment valued at \$356,000 was donated to a number of CAM programs (Table 5). A number of other industrial companies contributed valuable samples of materials for study in CAM programs, samples which are not readily available in the commercial market.

PROGRAM	COMPANY	EQUIPMENT DONATED	ESTIMATED VALUE
Catalysis	Perkin-Elmer	Components of ESCA and SIMS analytical systems	\$300,000
Catalysis	Chevron Research Company	Fourier Transform Infrared Spectrophotometer	\$50,000
Polymers and Composites	Rheometrics, Inc.	Components of a constant stress rheometer	\$6,000

TABLE 5
EQUIPMENT DONATED

Technology Transfer

Technology transfer occurs by several routes. Industrial visits, research contracts, and industrial fellowships have been discussed above. Research collaborations are reviewed in the individual research program sections in this report. All CAM work is published in the open literature; bibliographies containing the 137 articles in books, journals, and conference proceedings, 22 theses, 121 invited papers, 111 contributed papers, and 55 journal articles submitted for publication are to be found at the end of each program section. Finally, 18 of

the 26 graduate students who obtained their Ph.D. or M.S. degrees in CAM Programs are now employed in industrial laboratories (Table 6), bringing background and experience acquired at LBL to these companies. Six more have accepted faculty positions at Yale University, Wellesley College, University of Maine, Michigan Technological University, Diablo Valley College, and AJU University, Republic of South Korea. Another is working at Lawrence Livermore National Laboratory. Other graduates are continuing their education. Of the six postdoctoral associates who completed their training at CAM two have accepted faculty positions, at Lund University and Harvard University, three are working in industry at IBM and at Physical Sciences Incorporated, and one is continuing his education at Trinity College.

NAME	INSTITUTION
Graduates	
J. Armstrong	Faculty, Diablo Valley College
R. Berg	Faculty, Wellesley College
D. Bousefield	Faculty, University of Maine
J. Cain	AT&T Bell Laboratories
G. Caneba	Faculty, Michigan Technological University
S. Cheung	Ford Microelectronics Incorporated
M. Levin	Shell Development Company
G. Lipscomb	Dow Chemical Company
H. Mamin	CAM Postdoctoral Associate; IBM
D. Marinaro	Aluminum Company of America (Alcoa)
J. Millar	Faculty, Yale University
R. Moore	AT&T Bell Laboratories
N. Naito	G.T.E.
L. Parechianian	Kopin Corporation
G. Ranhotra	United Catalysts Incorporated
J. Schoenholtz	Eastman Kodak Company
G. Sikes	McDonnell Douglas
M. Smidebush	Strategic Yields
M. Strum	Lawrence Livermore National Laboratory
M. Tabache	European Space Agency
A. Thayer	AT&T Bell Laboratories
H. Tom	AT&T Bell Laboratories
H. Tsai	Engineering Mechanics Research Corporation
R. Walburg	National Semiconductor Corporation
S. Werner	Failure Analysis Association
J. Yoo	Faculty, AJU University, Republic of South Korea
Postdoctoral Associates	
D. Abraham	IBM
C. Cronin	Trinity College
D. Kaufman	Physical Sciences Incorporated
H. Mamin	IBM
P. Omling	Faculty, Lund University
D. Vanderbilt	Faculty, Harvard University

TABLE 6

CAM GRADUATES

Lawrence Berkeley Laboratory Figure Identification Numbers

Surface Science and Catalysis

Figure

1. XBL 875-8133
2. XBL 875-8134
3. XBB 867-5598
4. XBL 875-8135
5. XBL 863-1186
6. XBL 875-8136

Electronic Materials

Figure

1. CBB 860-8412
2. XBB 869-7831
3. XBL 8511-4633
4. XBB 868-6941
5. XBL 875-8137
6. XBL 8611-4479
7. XBL 863-1067
8. XBL 868-3142

Ceramic and Metal Interfaces

Figure

1. XBL 873-1182
2. XBL 875-2388
3. XBL 873-1185
4. XBL 873-1184 (*top*)
XBB 860-10028 (*bottom*)
5. XBB 850-9586 (*left*)
XBL 875-2389 (*right*)
6. XBB 875-4230 (*left*)
XBL 875-2390 (*right*)
7. XBL 873-1183 (*top*)
XBB 850-9591 (*bottom*)

Structural Materials

Figure

1. XBL 852-1090
2. CBB 860-8674
3. XBL 858-6543A
4. XBB 858-5979
5. XBL 875-8138
- 6a. XBB 864-2521
- 6b. XBB 864-2524

Structural Materials (continued)

Figure

7. XBL 875-8139
8. XBB 869-7448
9. XBB 868-6026
10. XBL 875-8140
11. CBB 868-6344
12. XBL 875-8141
13. XBL 875-8142
14. XBB 874-2855
15. XBL 875-8143

Instrumentation for Surface Science

Figure

1. XBB 866-4991
2. XBB 866-4979
3. XBB 867-5753
4. XBL 859-6610
5. XBL 865-1913
6. XBL 869-7736
7. XBL 861-7480
8. XBL 868-8916

Polymers and Composites

Figure

1. XBL 875-8144
2. XBL 875-8145
3. XBL 875-8146
4. CBB 850-10077
5. XBB 869-7163
6. XBL 875-8147
7. CBB 872-1383
8. XBL 874-1577
9. XBL 875-8148
10. XBL 875-8149

Industry Participation

Figure

1. XBC 866-5413